XVIII. *On the Absorption and Dialytic Separation of Gases by Colloid Septa.*
By Thomas Graham, *F.R.S., Master of the Mint.*

PART I.—ACTION OF A SEPTUM OF CAOUTCHOUC.

Mixed gases must differ considerably in diffusibility and specific gravity, in order to separate from one another to any great extent in their molecular passage into a vacuum through a porous septum, such as the plate of graphite or the walls of an unglazed earthenware tube. The agency of atmolysis is therefore very limited in parting the oxygen and nitrogen of atmospheric air—gases which differ so little in density from each other.

Substances existing in the liquid condition often admit of being separated much more fully than gases, by the proper use of dialytic septa in addition to the agency of liquid diffusion.

Evidently there cannot be anything like the dialysis of gases; for dialysis involves the passage of a substance through a septum composed of soft colloid matter, such as must be wholly destitute of open channels, and therefore be impermeable to gas as such. Still liquid dialysis may be imported into the treatment of gases, in consequence of the general assumption of liquidity by gases when absorbed by actual liquids or by soft colloids. Water when charged with air holds liquid oxygen and nitrogen in solution; and the latter substances then become amenable to liquid diffusion and dialysis, and so penetrate animal membrane in the act of respiration.

A considerable time ago Dr. Mitchell of Philadelphia discovered a power in gases to penetrate india-rubber in a thin sheet, or in the form of the little transparent balloons which Dr. Mitchell was the first to prepare from that substance. He remarked in particular that such balloons collapse sooner when inflated with hydrogen than with atmospheric air, and still sooner when filled with carbonic acid; and he connected the latter fact with the observation that a solid piece of india-rubber is capable of absorbing its own volume of carbonic acid when left long enough in the pure gas. By means of a proper arrangement, Dr. Mitchell found that various gases passed spontaneously through the caoutchouc membrane, *when there was air on the other side*, with different degrees of velocity. "Ammonia transmitted in 1 minute as much as sulphuretted hydrogen in $2\frac{1}{2}$ minutes, cyanogen in $3\frac{1}{4}$ minutes, carbonic acid in $5\frac{1}{2}$ minutes, nitrous oxide in $6\frac{1}{2}$ minutes, arsenietted hydrogen in $27\frac{1}{2}$ minutes, olefiant gas in 28 minutes, hydrogen in $37\frac{1}{2}$ minutes, oxygen in 1 hour and 53 minutes, carbonic oxide in 2 hours

and 40 minutes." The rate of penetration of nitrogen appeared to be even slower than that of carbonic oxide*.

It will be observed that those gases penetrate most readily which are easily liquefied by pressure, and which are also "generally highly soluble in water or other liquids." The memoir of Dr. MITCHELL was ably commented upon, shortly after its publication, by Dr. DRAPER of New York, who also added many new observations on the passage of both gases and liquids through membranous septa†. These early speculations, however, lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomena—namely, that gases undergo liquefaction when absorbed by liquids and such colloid substances as india-rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view.

Dr. MITCHELL was led to infer, from a single casual observation, that rubber expands in volume when carbonic acid is absorbed—a result to be expected from the porosity of the solid mass, then assumed in explanation of the penetrativeness of gaseous fluids. But on placing 50 grms. of thin sheet rubber, 0·6 millim. in thickness, in carbonic acid over mercury, it was seen that the rubber gradually absorbed 0·78 volume of gas in twenty-four hours at 15°, of which 0·7 volume was taken up in the first hour. The mass of rubber was previously measured with care by the displacement of mercury in a specific-gravity bottle, and again when the rubber was charged with carbonic acid; it gave the same displacement of mercury within a hundredth of a gramme. No measurable change in the bulk of the rubber, therefore, had occurred. It may be added that the absorbent power of vulcanized rubber for carbonic acid appears to be less than that of rubber in its natural state, being found only 0·57 volume in a comparative experiment.

The penetration of rubber by gases may be illustrated by their passage into a *vacuum*, as well as into an atmosphere of another gas in Dr. MITCHELL's experiments. The diffusiometer, consisting of a plain glass tube of about 22 millims. in diameter and nearly a whole metre in length, closed at the upper end by a thin plate of stucco and open below, is taken advantage of in such experiments. A thin film of rubber from a small balloon is stretched over the upper end of the tube, where it is supported by the stucco plate, bound with copper wire, and cemented at the edges in contact with the glass with gutta percha softened by heat. If the tube be now filled with mercury and inverted, a Torricellian vacuum is obtained above, into which the air of the atmosphere gradually penetrates, passing through the film of rubber and depressing the mercurial

---

* "On the Penetrativeness of Fluids," by J. K. MITCHELL, M.D.—Philadelphia Journal of Medical Sciences, vol. xiii. p. 36 ; or Journal of the Royal Institution, vol. ii. pages 101 and 307: London, 1831.

† A Treatise on the forces which produce the organization of Plants, with an Appendix containing several Memoirs on Capillary Attraction, Electricity, and the Chemical Action of Light, by JOHN WILLIAM DRAPER, M.D.

column in the tube. In order to compare the penetration of different gases, a hood of thick vulcanized rubber, provided with a small entrance- and exit-tube for gas (such as is often used in gas experiments), is placed over the upper end of the diffusiometer described, and cemented to it by means of fused gutta percha. The gas to be operated upon can thus be conveyed from the apparatus in which it is generated, or from a gaso-meter in which the gas is stored, into the hood or upper chamber of the diffusiometer, and the excess of gas supplied be allowed to escape into the atmosphere by the exit-tube of the hood. The stucco plate used as a support to the film of rubber is so highly porous as not to add sensibly to the resistance experienced by the gases in passing through the rubber, and, having no absorbent power of its own, may be left entirely out of consideration.

A comparison was made of the passage through the rubber film, on the same day, of carbonic acid, hydrogen, oxygen, and nitrogen; barom. 773 millims., therm. 23° to 23°·5 C. The time during which the mercurial column fell in the diffusiometer from 748 to 723 millims. was noted in seconds, and also from 723 to 698 millims. The gases were all care-fully dried.

TABLE I.—Passage of Carbonic Acid in seconds.

Height of mercurial column in diffusiometer.	Experiment 1.	Experiment 2.	Experiment 3.
millims. 748 723 698	$107''$ 143	$102''$ 138	$102''$ 138
	250	240	240

The passage of carbonic acid thus exhibited will be found to be considerably more rapid than those of hydrogen and the two other gases which follow:—

TABLE II.

Height of mercurial column in diffusiometer.	Passage in seconds,					
	of Hydrogen.		of Oxygen.		of Nitrogen.	
	Experiment 1.	Experiment 2.	Experiment 1.	Experiment 2.	Experiment 1.	Experiment 2.
millims. 748 723 698	$277''$ 316	$270''$ 323	$545''$ 727	$554''$ 722	$1413''$ 1832	$1428''$ 1850
	593	593	1272	1276	3245	3278

A single experiment, made at the same time on the passage of atmospheric air, gave times of 1318″ and 1524″ for the two stages, or 2842″ for the whole fall. The time of penetration of air is therefore intermediate between that of oxygen and nitrogen entering singly.

Although such numbers do not possess the close uniformity which appears in diffusion-

and transpiration-experiments, for reasons which will immediately appear, yet they give a comparative estimate of the penetrativeness of the different gases through rubber, which may be available for some practical purposes.

Upon another occasion carbonic oxide and marsh-gas (CH_4) were introduced into the comparison, the same film of rubber remaining upon the diffusiometer; barom. 768 millims., therm. 19°·5 C.

TABLE III.

Height of mercurial column in diffusiometer.	Passage in seconds,								
	of Carbonic oxide.		of Hydrogen.		of Carbonic acid.			of Marsh-gas (CH_4).	
	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 1.	Expt. 2.
millims. 748 723 698	1620″ 1920	1631″ 1924	435″ 505	434″ 511	125″ 170	119″ 169	117″ 172	803″ 1009	821″ 1045
	3540	3555	940	945	295	288	289	1812	1866

The results may be summed up by deducing the times in which a constant volume of the various gases is transmitted by the rubber, the time of passage of carbonic acid, which is the shortest, being taken as unity for the sake of comparison.

Penetration of rubber by equal volumes of Gas.

Time.

Carbonic acid 1

Hydrogen . . . . 2·470

Oxygen . . . . 5·316

Marsh-gas (CH_4) . . . . . . 6·326

Atmospheric air . . . . . . 11·850

Carbonic oxide . . . . 12·203

Nitrogen . . . . 13·585

Or, with the times taken equal, the volume of each gas which passes then expresses the velocity of penetration.

Penetration of rubber in equal times.

Velocity.

Nitrogen 1

Carbonic oxide . . . . 1·113

Atmospheric air . . . . . . 1·149

Marsh-gas (CH_4) . . . . . . 2·148

Oxygen . . . . 2·556

Hydrogen . . . . 5·500

Carbonic acid . . . . 13·585

Considering the circumstances in which the gases pass through the sheet of rubber into a vacuum, it is not to be expected that any relation will be found among the preceding numbers, as between the coefficients of diffusion in gases.   The first absorption of the gas by rubber must depend upon a kind of chemical affinity subsisting between the material of the gas and substance of rubber, analogous to that attraction which is admitted to exist between a soluble body and its solvent, conducing to solution. Carbonic acid being soluble in ether and volatile oils, it is not wonderful that it is also dissolved by the hydrocarbons of rubber.   The rubber being *wetted through* by the liquefied gas, the latter comes to evaporate into the vacuum, and reappears as gas on the other side of the membrane.   Now it is known that such evaporation is the same into a vacuum and into another gas, being equally gas-diffusion in both circumstances. It is not indispensable, therefore, to have a vacuum on one side of the rubber membrane as in the experiments detailed above.   A foreign gas will answer for the vacuum, as in the experiments of Dr. MITCHELL.

The numbers for the velocity of passage of the different gases in the last Table may be taken also as representing not remotely the relative absorption and liquefaction of the various gases by the substance of rubber.

The passage of gases through rubber is also illustrated by the rapid collapse of the little balloon when filled with carbonic acid gas, or even with hydrogen, or with marsh-gas, as compared with atmospheric air.   The converse fact is observed when the inflating gas is pure nitrogen : then the balloon is found to become further distended after a few hours, in consequence of more oxygen entering from the atmosphere without, than of nitrogen escaping from the balloon during the same time ; while the composition is being equalized on both sides of the membrane, and the gas within the balloon is finally of the same composition as the external air.   A rubber balloon filled with nitrogen was found, when roughly gauged, to increase in diameter from 132 to 136 millims. in the course of twenty-four hours.   On the other hand, a balloon filled with pure oxygen fell in the same time from 150 to 113 millims. in diameter.

In forty-eight hours a balloon filled with hydrogen 154 millims. in diameter contracted to 87 millims., and then contained 250 cub. centims. gas, of which 53 cub. centims. were absorbed by pyrogallic acid and potash, showing the presence of 21·2 per cent. of oxygen, or sensibly the same proportion as in the external atmosphere.

If the upper end of a diffusiometer be closed by a thin sheet of rubber, and the instrument standing over mercury be filled with hydrogen gas, a contraction is observed to take place slowly, but to a greater extent ultimately than could be due to the diffusion of hydrogen as a gas.   Beginning with 249 volume divisions of gas in the tube, the rise of the mercurial column, or reduction of volume, was 1·5 division in the first hour, 1·5 division in the second hour, 2·0 in the third hour, 3 in the fourth hour, and 51 divisions in the first twenty-four hours taken together.   Then the rise in the following successive days was 42, 59, 37, 29, 13, 5, 1, 0·5, 0·5 (in two days), and 0·0, the original volume of 249 volumes of hydrogen being finally replaced by 53 volumes of atmospheric air ; barom.

747 millims., therm. 21°·1. The ultimate replacing volumes are here as 1 to 4·7. In gas-diffusion they are as 1 to 3·8.

A balloon filled with air subsided in forty-eight hours from 150 to 147 millims. in diameter, from the mechanical effect alone of the elasticity of the membrane in compressing the enclosed gas. These little balloons vary from 0·75 to 1 grm. in weight. Supposing the form to be truly spherical, a balloon of 150 millims. in diameter would have a surface of 0·0706 square metre (5·905 inches in diameter and 0·08454 square yard of surface). Supposing the balloon to be 1 grm. in weight, the thickness of the membrane will be $\frac{1}{70·686}$ of a millim., with a specific gravity $=1$, or $\frac{1}{76·01}$ of a millim., with a specific gravity $=0·93$, the admitted density of pure rubber. This last is a thickness of $\frac{1}{1930·6}$ of an inch, or it would require nearly 2000 such films, laid upon each other, to form the thickness of a single inch. Yet such a film of rubber appears to have no porosity, and to resemble a film of liquid in its relation to gases—differing entirely in this respect from a thin sheet of paper, graphite, earthenware, or even gutta percha, as will appear hereafter. These last enumerated bodies appear all to be pervaded by open channels or pores, sufficiently wide to allow gases to be projected through by their own proper molecular movement of diffusion. But liquids and colloids have an unbroken texture, and afford no opportunity for gaseous diffusion. They form even in the thinnest film an impervious barrier to gas.

The penetration of rubber is much affected by temperature, and apparently in two different ways at the same time. An increase of temperature no doubt renders all gases less easily liquefied by pressure, and consequently less considerably absorbed by any liquid or colloid. But such an influence of heat appears to be counteracted in rubber by the tendency of that colloid to become more soft when heated, and to acquire more of liquid and less of solid properties. Certainly the rubber film becomes more and more permeable to gases as the temperature is elevated, within a moderate range. This was distinctly observed in operating with silk cloth varnished on one side with rubber, such as is sold as a waterproof material. Without anticipating a detail of the experiments, it may be stated in general terms that the same specimen of rubber was penetrated by air from the atmosphere passing into a vacuum, at the following rates per square metre of surface :—

At   4° C., by 0·56 cub. centim. of air in 1 minute.
At 14° C., by 2·25   „   „   „
At 60° C., by 6·63   „   „   „

The volumes of gas are all reduced to barom. 760 millims. and therm. 20° C.

Such numbers are probably not strictly constant; for it appears that the effect of temperature upon rubber is much influenced by the length of time that the temperature is continued, the change in degree of softness with change of temperature requiring hours, or even days, fully to complete it. The rigidity of rubber under cold and its softening under warmth are well known to take place in a slow and gradual manner.

With the softening of rubber by heat, the *retentive* power of that substance for gases

appears to be modified. Soft rubber, first charged with carbonic acid at 20°, and then made rigid by cold, appeared to lose its carbonic acid, when afterwards freely exposed to air, less rapidly than the same rubber equally charged but exposed from the first in its soft condition. The quantity of carbonic acid retained in the former case was 10·76 per cent., and in the latter 7·08 per cent. of the volume of the rubber, after a similar exposure of forty-eight hours. This point, although not sufficiently examined, is alluded to here on account of the analogy which appears to hold between rubber and the malleable metals in a power to absorb a gas when they are softened by heat, and to retain the same gas with great tenacity when they are afterwards made rigid by cold.

The condensation of oxygen gas by masses of solid rubber punched out of a block was made the subject of observation, by placing 50 grms. of that substance within a jar of oxygen standing over mercury during a period of several days. From the rubber afterwards there was extracted, by the action of a vacuum continued for twenty-one hours, 6·21 cub. centims. of gas; of which 3·67 cub. centims. were oxygen, 0·14 carbonic acid, and the remainder chiefly nitrogen. Taking the bulk of the rubber at 53·8 cub. centims., the oxygen absorbed amounts to 6·82 per cent. of the volume of the rubber. Oxygen then may be regarded as fully twice as soluble in rubber as the same gas is in water at the ordinary temperature. No experiment was made at a higher temperature; but as the penetrativeness of rubber is much increased by heat, the presumption is that the solubility of gases in rubber is increased in the same degree.

More than one attempt was made to identify the presence of free hydrogen in the substance of rubber after being kept in that gas for some time, but with a negative result. The absorbed hydrogen may be too easily dissipated, owing to its extreme volatility.

Dialytic separation of Oxygen from Atmospheric Air, (1) *by means of other gases,* (2) *by means of a vacuum.*

1. A balloon of rubber filled with *hydrogen* and exposed to the atmosphere, gradually loses the former gas, which is finally replaced by a considerably smaller volume of air, presenting a deceptive resemblance to the diffusion of hydrogen gas into air. When the progress of the entrance of air was observed at different stages of the exchange, it appeared that after three hours, when the balloon had fallen from 150 to 128 millims. in diameter, the composition of its contents was—

Oxygen . .	8·98	41·6
Nitrogen . .	12·60	58·4
Hydrogen . .	78·42	
	100·00	100·0

Setting aside therefore the hydrogen still remaining, the balloon now contained a portion of a mixture of oxygen and nitrogen in the proportion of 41·6 volumes of the former to 58·4 volumes of the latter. This was the largest proportion of oxygen to the

nitrogen observed; for the former gas has a tendency to flow back again to the external atmosphere when the hydrogen becomes small in volume; and the proportion of oxygen becomes eventually no higher than 21 per cent. of the whole gases remaining in the balloon, including the hydrogen. Thus after six hours the proportion of oxygen was 33·63 to nitrogen 66·37 volumes, and after twenty-four hours oxygen 26·48 to nitrogen 73·52 volumes, the hydrogen constantly diminishing at the same time.

The entrance by infiltration of atmospheric air into a balloon of rubber inflated with *carbonic acid* gas brings us still nearer to a practical dialytic separation, as the carbonic acid can be withdrawn entirely by means of caustic alkali, after a certain time has elapsed, and the infiltered air enriched with oxygen be dealt with by itself. A balloon containing carbonic acid, when placed in the atmosphere, was reduced in four hours from 160 to 90 millims. in diameter, and it had now acquired 199 cub. centims. of gas not dissolved by alkali. This gas was capable of reviving the combustion of wood burning without flame, and was found to consist of

Oxygen . . . . . 37·1 vols.
Nitrogen . . . . . 62·9 „
———
100·0

To produce this concentration of oxygen, it is quite necessary that the operation be interrupted at an early stage, as was done in the last experiment; otherwise the oxygen diminishes again in proportion to the nitrogen, falling at last to the normal proportion of 21 per cent. as in the external air. Thus a balloon inflated by carbonic acid to 150 millims. in diameter, was found to lose nearly all its carbonic acid in the course of twenty-four hours. It gave 150 cub. centims. of gas after treatment with caustic potash. This was air of the composition,

Oxygen . . . . . 22·6
Nitrogen . . . . . 77·4
———
100·0

and exhibited therefore no material augmentation in the proportion of oxygen.

It may be inferred, from the familiar fact that air dissolved in water contains so high a proportion as 30 per cent. of oxygen, that if carbonic acid gas were divided from atmospheric air by a film of *water*, the former gas would come to be charged through the film with air bearing the same high proportion of 30 per cent. of oxygen. But it is not easy to imitate this experiment unless the dividing film is supported by a membrane of some sort. The air from the atmosphere, which entered a fresh ox-bladder preserved humid and inflated with carbonic acid, was found to possess 24·65 per cent. of oxygen to 75·35 of nitrogen, which is but a small increase in the proportion of oxygen. But the thickness of the membrane here was too great, and other circumstances of the experiment were unfavourable.

A balloon of rubber inflated to 150 millims. in diameter with carbonic acid was

submerged in water, at 22° C., for forty-eight hours.   Only a small portion of carbonic acid remained in the residual gas, which, after being washed with potash, consisted of

$$\begin{array}{ll} \text{Oxygen} & 25\cdot77 \\ \text{Nitrogen} & 74\cdot23 \\ \hline & 100\cdot00 \end{array}$$

2. With the colloid septum properly supported, as by a stucco plate in the diffusiometer covered by a film of rubber (p. 400), a considerable separation of mixed gases can be effected.   The constituents of atmospheric air appear to be carried through a film of rubber into a vacuum, nearly in the same relative proportion as the same gases penetrate singly (p. 402).   The velocities of nitrogen and oxygen passing separately were observed to be as 1 to 2·556, and hence by calculation,

$$\begin{array}{lll} \text{Oxygen} & 21\times2\cdot556=53\cdot676 & 40\cdot46 \\ \text{Nitrogen} & 79\times1 \quad\; =79 & 59\cdot54 \\ \hline & & 100\cdot00 \end{array}$$

Hence air dialyzed by the rubber septum should consist of 40·46 oxygen and 59·54 nitrogen in 100 volumes.   Now air from the atmosphere was found to enter the vacuum of the 48-inch diffusiometer-tube, through a disk of rubber 22 millims. in diameter, to the amount of 3·48 cub. centims. in twenty-one hours, under the pressure of the atmosphere; therm. 23° to 24° C.   Of the 3·48 cub. centims. of gas so collected, 2 cub. centims. were absorbed by pyrogallic acid and potash, representing 42·53 *per cent. of oxygen* in the dialyzed air.   Here the gas was transferred from the diffusiometer for examination by depressing the diffusiometer in mercury, and using a very narrow tube of rubber as a gas-siphon communicating between the gas in the diffusiometer and a jar inverted in the mercurial trough.   The elastic tube is first filled with mercury, and, being of considerable length, a portion of it is drawn repeatedly through the fingers so as to throw the mercury and aspirated gas into the collecting receiver.   The transference of gases in such circumstances may also be effected with much advantage by means of the vacuum-tube invented by Dr. HERMANN SPRENGEL, as will immediately be shown.
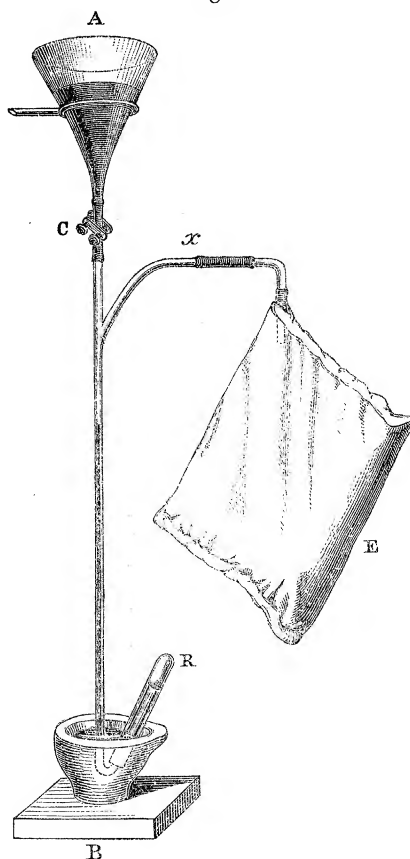
The process of dialytic separation by means of a rubber septum may be varied in three points,—(1) in the condition of the rubber septum, which may be a film of rubber formed from caoutchouc varnish as well as from distended sheet rubber; (2) in the nature of the support given to the septum, which may be a backing of cotton cloth or of silk (common waterproof cloth prepared by means of caoutchouc varnish, in short), as well as a plate of stucco, earthenware, or wood; and (3) in the means had recourse to for sustaining a vacuum, or at least a considerable degree of exhaustion, on one side of the dialytic septum, while atmospheric air, or any other gaseous mixture to be dialyzed, has access to the other side of the same septum.   Or the air to be dialyzed may be compressed on one side of the septum, and left of the usual tension on the other side, inequality of tension on the two sides of the septum being all that is required to induce penetration.

The pneumatic instrument of Dr. SPRENGEL (fig. 1) is peculiarly applicable to researches of the present kind.   Indeed without the use of his invention some parts of the inquiry would have been practically impossible*.   The instrument was originally offered by the inventor as the means of producing a vacuum*, or as an air-pump. But by bending the lower end of the straight fall-tube, the instrument may be further made to deliver gas into a receiver, and be used with advantage as the means of transferring small volumes of gas from one vessel to another.

Fig. 1.

While the mercury in the funnel A is allowed to flow downward into the barometer-tube CB, of $2\frac{1}{2}$ millims. in diameter, by relaxing the clamp upon the adapter tube of rubber at C, a connexion is also made with the close receiver to be exhausted, such as an air-tight bag E, by means of the branch tube x. The air in E, gaining access to the Torricellian vacuum, is swept on by the falling mercury, and delivered below into the small gas-receiver R, previously filled with mercury and inverted over mercury in the mortar B below.   The principal difficulty in obtaining a good vacuum in E by means of this apparatus arises from the necessity of joining the glass tubes in more than one place by means of adapter tubes of rubber.   The directions given by Dr. SPRENGEL on this point require to be closely followed :—" The connexions between the glass tubes are made of well-fitting black vulcanized caoutchouc tubing, sold under the name of French tubing.   This is free from metallic oxides, which render the tubing porous.   Besides this all these joints are bound with coils of copper wire, which is easily accomplished with a pair of pliers."   The joints should also be coated with gutta percha liquefied by heat, or with fused rubber.   An exhausting-syringe, or air-pump, may often be used with advantage to begin the exhaustion, and to withdraw the greater bulk of the air, if the receiver is large, the Sprengel tube being reserved to complete the exhaustion.   The vacuum appears to be as perfect as can be formed in a barometer-tube filled with unboiled mercury, and to come within 1 millim. of the barometric gauge.

The following modifications of the experiment exhibit the dialytic action of caoutchouc in its various forms.

* Researches on the Vacuum, by HERMANN SPRENGEL, Ph.D., Chemical Society's Journal, ser. 2, vol. iii. p. 9 (January 1865).

1. *India-rubber between double cotton cloth vulcanized.*

This was a common elastic carriage-bag 18 inches by 15. The surface of both sides amounted to 0·3482 square metre. The bag was pressed flat by the hands, and still further exhausted by means of SPRENGEL'S tube. After all the contents of the bag were extracted and the collapse complete, the Sprengel tube began again to throw out air in a slow but exceedingly regular manner. A small portion of sawdust, or of sand, introduced beforehand into the bag, appeared to be useful in preventing the sides coming together too closely, but was not essential. The air thus extracted from the bag in one hour amounted to 15·65 cub. centims., or sensibly 1 cubic inch; therm. 23° to 24° C. Such dialyzed air, from three successive experiments of one hour each, contained 38, 40·3, and 41·2 per cent. of oxygen, the inferior proportion of oxygen in the earlier experiments being no doubt due to a small residue of undialyzed air remaining in the bag before exhaustion. This dialyzed air rekindled glowing wood, so as to illustrate the direct separation of oxygen gas from atmospheric air. For the purposes of combustion, it may be viewed as air from which one-half of the inert nitrogen has been withdrawn.

It will be convenient to express the permeability of the colloid septum with uniform reference to a square metre of area, and to an hour, or to a single minute of time. Here, for a square metre of cloth, the passage of air amounted to 44·95 cub. centims. (3 cubic inches nearly) per hour, or to 0·749 cub. centim. per minute.

The view which the observation suggests of the nature of such an air-tight fabric is, that it may be truly impenetrable to air when the composition and tension of the air are the same on both sides of the cloth; but it is penetrable when a vacuum or a reduced state of tension is maintained on one side of the cloth and not on the other. The compression of the air confined in a bag would no doubt have a similar effect, and then the flow would be in an outward direction. But there is no evidence of a porous structure in the varnished cloth. The gases of atmospheric air would pass through actual openings according to the law of gaseous diffusion, which favours the nitrogen or lighter gas, while it is the oxygen which is found to pass through the material most readily in these experiments. The imbibition of the liquefied gas by the substance of the rubber, with the subsequent evaporation of this liquid into the vacuum on the other side, is all the explanation required.

2. *Vulcanized india-rubber tubing.*

A stout caoutchouc tube with an external diameter of 13 millims. (half an inch), an internal diameter of 9 millims., thickness of 2 millims., and length of 3·658 metres (4 yards) was exhausted, one end being closed and the other end connected with the Sprengel pump. The gas collected in thirteen hours amounted to 11·25 cub. centims.; therm. 20° to 23° C. This gas contained 37·8 per cent. of oxygen. The gaseous penetration is not great in so thick a tube, and there is reason to fear the influence of gaseous diffusion to a small extent. The admission of air would be equally sensible if

the tube were occupied by coal-gas, or any other foreign gas, instead of being vacuous. As the inner surface of the tube amounted to 0·1034 square metre and the passage of air to 0·8653 cub. centim. per hour, the passage for a square metre would be 8·37 cub. centims. per hour, or 0·14 cub. centim. per minute. The rate of penetration through the tube-walls appears to be one-fifth of what was found for the rubber cloth.

3. *Sheet rubber,* 1 *millim. in thickness.*

Although an increased thickness was no doubt attended by slowness of passage, it was of interest to observe whether the proportion of oxygen per cent. might not at the same time be varied. The sheet used was still, however, as thin as the manufacturer could succeed in cutting from a solid cylinder of wrought rubber by the usual method. The rubber was not vulcanized. The sheet of rubber was made into a bag having 0·149 square metre (231 square inches) of surface, a double thickness of felted carpet being placed within the folds of rubber. A glass quill tube, cemented to the bag, communicated with the interior of the cavity, and was connected at the other end with SPRENGEL's tube. After the first exhaustion of the gaseous contents of the bag, for which the aid of an exhausting syringe or air-pump is useful, air continued to infiltrate through the sheet rubber, but very slowly. Of the dialyzed air 11·45 cub. centims. were collected in four hours. This air contained 41·48 per cent. of oxygen, with a sensible trace of carbonic acid. The penetration for a square metre amounts to 19·2 cub. centims. of air per hour, or 0·32 cub. centim. per minute.

The same bag, left exhausted for eighteen hours, was found afterwards to yield at once 41·6 cub. centims. of air, containing 40·3 per cent. of oxygen, which had accumulated in the cavity of the bag; therm. about 20° C.

From a larger bag of similar thin sheet rubber, having a surface of 640 square inches, distended by ten or twelve ounces of sawdust, 21·35 cub. centims. of dialyzed air were obtained in one hour; barom. 761 millims., therm. 19°·5 C. This dialyzed air appeared to consist of

Oxygen	41·80
Carbonic acid	0·94
Nitrogen	57·26
	100·00

It does not appear, then, that the increased thickness of the rubber septum tends to increase the proportion of oxygen in the dialyzed air, while this thickness causes the passage to be proportionally slower. The oxygen appears to attain, but never to exceed, at 20° C., the proportion of 41·6 to 58·4 nitrogen.

The thick rubber brings notably into view the carbonic acid of the air. The small proportion of this gas in air is probably increased in all experiments with the rubber septum, however thin. It was observed to rise so high in a small crowded room, as to negative the inflaming action of the oxygen on smouldering wood. But rubber appears

to have a power to charge itself gradually from atmospheric air with about half per cent. of its volume of carbonic acid. This carbonic acid, accumulated in thick sheet rubber, appears again to be carried on by the other gases imbibed in a dialytic experiment.

4. *Thin Balloons of india-rubber.*

These little balloons were made available for the dialytic passage of air into a vacuum by filling them with sifted sawdust through a funnel, an operation which requires some address. The balloon collapsed upon the sawdust, which formed an interior ball, the sides of rubber still retaining a thickness of about one-fiftieth of a millimetre. The rubber is not vulcanized. Such a ball, of which the original rubber weighed 0·76 grm., still remained 95 millims. in diameter after the air was exhausted. It was found, when exhausted, to admit 19·6 cub. centims. of dialyzed air in forty-one minutes; barom. 579 millims., and therm. 19° C. The same air possessed 41·32 per cent. of oxygen. The ball had a surface of 0·0283 square metre, and it dialyzed 0·48 cub. centim. of air in one minute. For a square metre of surface this is a passage of 16·9 cub. centims. per minute. The passage therefore is about fifty times as fast as through a sheet of rubber of 1 millim. in thickness, while the high proportion of oxygen is sensibly the same. Such a ball was found to dialyze air in the same manner for more than a month, if protected from mechanical injury.

Three such balls, each containing twenty-three ounces of sifted sawdust, were made to act together, by connecting them with three dependent branches from the same horizontal glass tube. The horizontal tube was connected at one end with an ordinary air-pump which produced a good vacuum by thirty or forty strokes of the piston. The other end of the horizontal glass tube was attached to a good Sprengel apparatus of the largest admissible size, constructed by Messrs. ELLIOT of the Strand. It was found, however, that the dialyzed air entered rather more rapidly than it could be extracted by a single Sprengel apparatus. This was at the rate of 5 cub. centims. in one minute; therm. about 20° C. The dialyzed air contained 40·5 per cent. of oxygen.

The greatest amount of aërial dialysis per square metre was obtained by means of a rubber bag, larger than usual, and weighing 1·55 grm. When filled with the sawdust and exhausted, this bag still remained of 143 millims. in diameter, and with a surface therefore of 0·0642 square metre. The air which passed through amounted to 17·05 cubic centims. in ten minutes; therm. about 20°. This air gave 40·7 per cent. of oxygen. For a square metre of surface, this is the passage of 26·5 cub. centims. per minute, the highest which has as yet been observed.

In the thin transparent envelope of the little balloon of rubber we have a colloid substance in the most favourable form yet applied to the dialysis of mixed gases. But there is still much room for improvement in the mode of using the thin septum in question. The balls are apt to contract considerably, owing to their elasticity, in the operation referred to, of filling them with sawdust; their walls become at the same time thicker and less quickly pervious. A mode of destroying the elasticity of the membrane when in its

most attenuated condition, so that the balloon might be cut open and the membrane spread out without shrinking, would be very useful. Instead of depending upon the interior support of sawdust, the membrane could then be stretched over a more convenient frame to support it, of thin porous deal, of unglazed earthenware, and even of a felted fabric, or several thicknesses of unsized paper supported by a slight frame, so as to form a hollow cavity that admitted of being exhausted of air. The attention of manufacturers of rubber might be advantageously directed to the preparation and proper support of the thinnest possible septa of that material.

The varnish of rubber which appeared to offer the best septum on drying, was a thin solution of rubber in 200 times its weight of chloroform. Four or five coats of this varnish required to be applied to a surface of wood, or of unglazed earthenware, to form an air-tight envelope. The film appeared to exceed in thickness the rubber balloons, and it dialyzed air less rapidly. But a better result may be expected at the hands of experienced manufacturers.

The thin rubber membrane of the balloons was stretched over the ends of glass tubes already closed with a plate of porous stucco—and also over the mouths of small glass bulbs or osmometers, closed with a disk of porous wood or of unglazed earthenware, and which presented a surface of one-hundredth of a square metre. The membrane of the balloon could only be applied while double; but after the covering was securely bound to the glass and cemented with fused gutta percha at the edges, the outer coating was torn off, so as to leave only a single thickness of rubber as the dialytic septum. A bulb of the kind described, when exhausted by a Sprengel pump, gave afterwards 16·36 cub. centims. of dialyzed air in two hours, containing by analysis 41·3 per cent. of oxygen, therm. 23° C.; in the following two hours, 17·35 cub. centims. of air, containing 42·6 per cent. of oxygen. This last is at the high rate, for a square metre of surface, of 14·46 cub. centims. per minute.

5. *Silk cloth varnished with rubber on one side, slightly vulcanized.*

This is a thin but close silk fabric, much used for waterproof garments. It appears also to be employed, when dyed of a fancy colour, in the preparation of artificial flowers and for other purposes. The silk cloth is of a single thickness; and the coating of rubber, which is of a black colour, appears on one side only. It is a much superior material to the ordinary cotton fabrics, which are double, with the two varnished sides pressed together, and is much more to be depended upon for being sound and free from pores than the "waterproof" cotton cloth. The silk cloth, however, should always be tested by examining air dialyzed by means of it. If the proportion of oxygen falls below 40 per cent., the silk is unsound at one or more spots. These spots may generally be discovered by wetting one side of the silk with a sponge and observing where the passage of water is indicated by a visible stain on the other side. The defective spot may be covered by a small disk of sheet rubber applied warm to the surface. Such varnished

silk, although not the most rapid in its dialytic action, was more convenient in use than any other septum hitherto tried.

The varnished silk stretched over a disk of porous earthenware (for support) closing the mouth of the small glass bell-jar or osmometer, which has an opening of one hundredth part of a square metre, gave 10 cub. centims. of dialyzed air in one hour, containing 42·2 per cent. of oxygen; barom. 767 millims., therm. 23°·5. For a square metre of surface this is a passage of 2·77 cub. centims. of air per minute.

A small bag, useful for experimental purposes, was constructed of a portion of the same varnished silk, 0·53 metre in length by 0·27 metre in width, which had therefore a surface of 0·143 square metre. The varnished side was turned inwards. Between the folds of the silk was placed a double thickness of common felt carpet or a piece of wadding, so as to occupy the interior of the bag. A glass quill tube also entered the bag to the depth of a few inches, and projected as much outside, so as to admit of being connected, by means of a sound adapter tube of French rubber, with a Sprengel pump, as shown in figure 1 (page 408). The edges of the silk cloth were cemented round by caoutchouc varnish, to a depth of 10 millims., so as to close the bag; and care was taken also to cement the glass tube well to the edges of the bag. When the silk bag is exhausted of air, it remains nearly flat, and feels hard like a piece of cardboard. Such an *air-dialyzer* is further improved by interposing a strong glass flask or bottle, of one or two litres in capacity, between the bag and the pump, so that both are exhausted of air at the same time. The flask must be strong enough to bear the full pressure of the atmosphere without breaking. An auxiliary air-pump, to produce the first exhaustion, cannot well be dispensed with where the space to be made vacuous is so considerable; the Sprengel tube is brought into action afterwards. The advantage gained by the vacuous flask, and even by the thick wadding placed within the bag, is that they form a magazine in which the dialyzed air can be allowed to accumulate for several hours or a whole day, and from which the air may afterwards be drawn quickly by the Sprengel tube for the purpose of experiment. A narrow glass receiver tube, which can be closed by the thumb, may be used to take 5 or 6 cub. centims. for an observation on the inflammation of a chip of wood in the highly oxygenated air. When the proportion of oxygen is under 33 per cent. the wood is not rekindled; but in the ordinary action of this dialyzer the oxygen is seldom found under 40 per cent. The best result is obtained when the exhaustion is within half an inch of the barometric vacuum. When the pressure was allowed to fall to one-half or one-third of an atmosphere, the proportion of oxygen was lessened by 2 or 3 per cent.

The action of heat and cold on the penetrability of rubber is considerable, as has already been stated. Operating with the dialyzing-bag described, without any intermediate flask, the volume of air collected in twenty minutes was 6·35 and 6·57 cub. centims. in two consecutive experiments; barom. 760 millims, therm. 20°. For a square the rate is 2·22 and 2·29, average 2·25 cub. centims. per minute. The proportion of oxygen was, in the first experiment 42·5, and in the second 41·66 per cent.

When the same dialyzing-bag was kept at a temperature of 60° C., the volume of air collected in seven minutes was 6·22 and 7·06 cub. centims. For the square metre this amounts to 6·21 and 7·05, mean 6·65 cub. centims. per minute. The passage of air through rubber is therefore almost exactly three times as quick at 60° as at 20° C.

Again, the dialyzing-bag was kept at 4° C. by being surrounded by ice and salt. The air now collected in seventy-two minutes was 5·78 and 5·77 cub. centims. in volume— for a square metre 0·56 cub. centim. per minute. The passage of air through rubber thus appears to be four times as slow at 4° C. as it is at 20°. The proportion of oxygen in the dialyzed air increased at the same time. In the two portions of air collected at 4° the oxygen was 46·75 and 47·43 per cent. The increase of oxygen at a low tempe-rature was confirmed in other experiments; but it appeared at the same time that the rubber was liable to acquire a true porosity to a slight extent when retained for some hours about 0° C. The rubber then allowed air to pass through it containing no more than 28 or even 23 per cent. of oxygen, and in volume still very small. The rubber has become rigid by the cold, and is now acting feebly as a porous substance, allowing a little gas-diffusion to take place through its substance. Such a condition, which is accidental to caoutchouc at a low temperature, appears to be constant with gutta percha, a harder material, at 20° C., and even higher temperatures.

A large bag of varnished silk with a surface of 1·672 square metre (two square yards) was found still more convenient. It was, however, rather beyond the exhausting-power of the largest Sprengel pump. It yielded in eight minutes, without any collecting-flask, 22, 21·55, and 21·5, mean 21·68 cub. centims. This was a supply of 2·71 cub. centims. per minute, and was at the rate, for a square metre, of 1·62 cub. centim. per minute. The supply would have been about a half more if the dialyzed air had not gained upon the pump. The air of the first and last observations contained respectively 41·89 and 41·85 per cent. of oxygen.

The usual proportion of oxygen in air dialyzed by rubber appears to be about 41·6 per cent.; and it may be described as atmospheric air deprived of one-half of its usual proportion of nitrogen. A single dialysis of air therefore carries the experimenter already halfway from air to pure oxygen as the final result. But the gain by a second dialysis could not be so great, as it would only withdraw one-half of the nitrogen that remained after the first operation, a third dialysis one-half of the nitrogen remaining after the second operation, and so on—each step of the concentration of the oxygen being obtained at a greater cost than the last, and the best conceivable result being only a good approximation. The practical problem which is suggested by the air-dialyzer is, to attain the means on a large scale of reducing to one-half, or so, the proportion of nitrogen in atmospheric air, to be applied to certain useful purposes.

6. *Percolation of air through gutta percha and other septa.*

Thin transparent sheets of a certain material represented as air- and water-tight are in common use. It is often spoken of as consisting of caoutchouc, but appears to have

a body of gutta percha, softened probably by a drying-oil. From its softness and thinness, this sheet of gutta percha appeared at first highly promising. But it appears not to be free from small apertures for any considerable surface. When a small sound portion was operated upon, air was found to percolate through it very slowly. In a tube diffusiometer of 1·3 metre in length and 20 millims. in diameter, closed at the top with this septum supported by stucco, the mercurial column fell from 28·7 to 22·625 inches in 18½ hours. The gas which had entered above the mercury measured 13·54 cub. centims., and was found to contain 20·2 oxygen to 79·8 nitrogen—a proof that the air had entered by gas-diffusion. The material is in fact of sufficient porosity to permit the molecular passage of gases in a slow manner.

Varnishes of gelatine and of drying-oil have been tried as dialytic septa, but hitherto without marked results.

PART II.—ACTION OF METALLIC SEPTA AT A RED HEAT.

Platinum.

The surprising passage of gases through the homogeneous substance of a plate of fused platinum or of iron at a red heat, lately discovered by MM. H. STE.-CLAIRE DEVILLE and TROOST, may possibly prove to be analogous in its mode of occurrence to the passage of gases through the rubber septum. At the same time it must be admitted that such an hypothesis as that of liquefaction can only be applied in a general and somewhat vague manner to bodies so elastic and volatile at an elevated temperature as the gases generally must be, and hydrogen in particular. Still some degree of absorbing and liquefying power can scarcely be denied to a soft or liquid substance, in whatever circumstances it may be found, with such a patent fact before us as the retention by fused silver of 18 or 20 volumes of oxygen at a red heat. It may safely be assumed that the tendency of gases to liquefaction, however much abated by temperature, is too essential a property of matter to be ever entirely obliterated.

A little consideration also shows that the absorption of gas by a liquid or by a colloid substance is not a purely physical effect. The absorption appears to require some relation in composition—as where both the gas and the liquid are hydrocarbons, and the affinity or attraction of solution can come into play. May a similar analogy be looked for, of hydrogen to liquid or colloid bodies of the metallic class?

With reference to the mechanical pores of a solid mass, liquids are probably more penetrating than gases. The former show often a power of adhesion to solids, while gases appear to be essentially repulsive. A degree of minute porosity is conceivable, which will admit a liquid, but may be impassable to a gas, even under its molecular movement of diffusion.

Finally, there is presented to us a bold and original conjecture by M. DEVILLE, in explanation of his own observations. It is clearly expressed in the following quotation taken from the last publication of M. DEVILLE on this subject:—

" La perméabilité de la matière est d'une nature toute différente dans les corps homogènes, comme le fer et le platine, et dans des pâtes plus ou moins discontinues, resserrées par la cuisson ou la pression, comme la terre à creuset, la plombagine, dont M. GRAHAM s'est servi dans ses mémorables expériences. Dans les métaux, la porosité résulte de la dilatation que la chaleur fait éprouver aux espaces intermoléculaires; elle est en relation avec la forme des molécules que l'on peut toujours supposer régulières, et avec leur alignement qui détermine le clivage ou les plans de facile fracture des masses cristallisées. C'est cet intervalle intermoléculaire que le phénomène de la porosité des métaux purs et fondus accuse avec une évidence éclatante, c'est aussi par ce phéno-mène qu'on peut espérer de calculer la distance des molécules solides aux températures élevées où les gaz peuvent s'y introduire."

A new kind of porosity in metals is imagined, of a greater degree of minuteness than the porosity of graphite and earthenware. This is an intermolecular porosity due entirely to dilatation. The intermolecular porosity of platinum and iron is not sufficient to admit any passage of gas at low temperatures, but is supposed by M. DEVILLE to be developed by the expansive agency of heat upon the metals, and to become sensible at the temperature of ignition. Such a species of porosity, if it exists, may well be expected to throw light on the distances of solid molecules at elevated temperatures, when gases introduce themselves. The ready passage through platinum of some gases, particularly of hydrogen, and the difficult passage of others render such molecular views the more remarkable.

The passage of hydrogen through the substance of heated platinum appears in its most simple aspect when the gas is allowed to make its way through the metal into a vacuous space. The experiment of M. DEVILLE, where a tube of platinum charged with nitrogen is placed within a large porcelain tube charged with hydrogen*, was modified by placing the platinum tube, closed at one end, in communication by the other (open) extremity with the Sprengel pump, so that a vacuum was substituted for the nitrogen. It was then easy to observe that a vacuum in the platinum tube was preserved for hours when the external gas admitted into the annular space between the porcelain and plati-num tubes was either atmospheric air or hydrogen at the natural temperature. The tubes being placed across an empty furnace, the latter was now lighted; and it was seen that, with air circulating outside the platinum, the vacuum remained undisturbed, even when the temperature of the tubes rose to a bright red heat. But when dry hydrogen was driven through the same annular space, the platinum, while continuing impermeable at all temperatures below a dull red heat, began to admit hydrogen to the vacuum as soon as the external porcelain tube became visibly red-hot. In seven minutes the Sprengel pump now delivered 15·47 cub. centims. of gas, of which 15·27 cub. centims. appeared, by explosion with oxygen, to be hydrogen.

In a repetition of the last experiment, hydrogen dried by sulphuric acid was again allowed to circulate in excess outside the platinum. After a vacuum was once obtained

* Comptes Rendus, vol. lvii. p. 965.

within the platinum tube, the gas delivered by the Sprengel pump, in the cold, during a period of forty minutes, amounted to no more than a bubble of the size of a pin-head, showing the tightness of the apparatus. The Sprengel pump being constantly kept in action, the tubes were now heated to redness, and then gradually to a temperature approaching a white heat. The gas delivered each five minutes was found to be 13, 15·5, 17·4, 16·9, 18·6 cub. centims. as the temperature rose. These volumes are referred to a temperature of 20° and barometer of 760 millims. The last observation gives a passage of 3·72 cub. centims. of hydrogen per minute. The platinum tube employed here was joined without solder, having been drawn from a mass of platinum which had been aggregated by fusion. It was similar in this respect to the tube employed by M. DEVILLE. The tube was 0·812 metre in length (32 inches) and 1·1 millim. in thickness, with an internal diameter of 12 millims. But only a portion of about 200 millims. (8 inches) of the tube were heated to redness in the furnace experiment. The inner surface of the heated portion has therefore an area of 0·0076 square metre. Hence one square metre of heated platinum delivers 489·2 cub. centims. of hydrogen per minute. This result admits of comparison with the passage of gases through a septum of rubber. In the most favourable circumstances, when the thin membrane of a rubber balloon was employed, the passage of air into a vacuum was at the rate of 26·5 cub. centims. per square metre in one minute. The passage of hydrogen may be taken as 4·8 times as rapid as that of atmospheric air, or at 127·2 cub. centims. per minute. But while the thickness of the platinum septum was 1·1 millim., that of the rubber film was only one-seventieth part of a millimetre. Hence we have the ultimate comparison :—

Passage of hydrogen gas in one minute through a septum of 1 square metre:

Through rubber 0·014 millim. in thickness, 127·2 cub. centims. at 20° C. ;

Through platinum 1·1 millim. in thickness, 489·2 cub. centims. at bright red heat.

If the permeation of hydrogen is due to the same agency in both septa, can the vast superiority of the platinum septum be connected with its greatly higher temperature ?

It was interesting now to turn from hydrogen to the passage of other gases through heated platinum. The experiments were all made in the same way, and at a full red heat. The temperature, it will be observed, was short of that at which the elements of water and carbonic acid are partially dissociated.

Oxygen and nitrogen.—Atmospheric air, which may be taken to represent both of these gases, was now allowed to flow through the annular space between the tubes, the interior platinum tube being kept vacuous as usual. In one hour the gas collected by the constant action of a Sprengel pump amounted only to 0·3 cub. centim. Hydrogen in the same time would have given 211 cub. centims. It is very doubtful, too, whether the trifling fraction of a centimetre of gas collected had all passed through the platinum ; a part (or the whole of it) may have entered by the joints of the apparatus. Platinum, then, cannot be said to be sensibly permeable to either oxygen or nitrogen, even at a full red heat.

Carbonic acid.—This gas was supplied from a bottle containing marble, by the action

of pure hydrochloric acid, the gas being afterwards washed with water and dried by sulphuric acid in its way to the exterior porcelain tube. In one hour the interior platinum tube yielded only three-tenths of a cubic centimetre of gas, of which, again, only an indeterminate small portion was condensed by baryta water and appeared to be carbonic acid. The passage of carbonic acid is therefore incalculably small at a full red heat.

Chlorine.—This gas, evolved slowly from a glass flask containing peroxide of manganese and hydrochloric acid, was washed by water, dried by sulphuric acid, and thrown as usual into the porcelain tube so as to occupy the annular space between the two tubes. A small tube containing slaked lime was interposed between the end of the platinum tube and the Sprengel pump, so as to absorb the chlorine, if any came through the substance of the platinum. After the tube had been heated for an hour, the lime was examined for chlorine, but did not contain a trace of that substance. A minute quantity of gas, probably air, amounting to 0·15 cub. centim., was collected during the time. Platinum, then, is not sensibly penetrated by chlorine at a red heat.

Hydrochloric acid, dried over sulphuric acid, was passed for one hour through the porcelain tube. About 0·5 cub. centim. of gas was collected from the platinum tube, which contained no hydrochloric acid and no free hydrogen. The ignited platinum, then, is not penetrated by hydrochloric acid; nor does it appear to dissociate the elements of that gas at the temperature of the experiment.

Vapour of water.—A stream of steam was carried for one hour through the porcelain tube. During that time half a cub. centim. of gas appeared to be drawn from the platinum tube, which gas contained no hydrogen. There is no evidence of the passage through the platinum of the vapour of water, nor of its decomposition.

Ammonia.—This gas appeared to be decomposed to a considerable extent in passing through the heated annular space, hydrogen passing freely at the same time through the ignited platinum. No trace of undecomposed ammonia, although the gas was transmitted in considerable excess, was discovered accompanying the free hydrogen found in the platinum tube. When the ammonia was evolved slowly, the quantity of hydrogen entering the platinum tube amounted to 16·4 cub. centims. in five minutes, or was sensibly the same as when pure hydrogen was carried through the annular space. Ammonia, then, appears to be incapable of penetrating the ignited platinum.

Coal-gas.—When coal-gas was carried through the porcelain tube, the following quantities of hydrogen came through the platinum in successive periods of twenty minutes each, 13·3 cub. centims., 5·2, and 8·8. The first portion, when exploded with oxygen, did not disturb baryta-water after condensation; 13·3 cub. centims. contained 13·16 cub. centims. of hydrogen. It appears, then, that the permeating gas was free hydrogen only, and that no compound of carbon present in coal-gas was capable of passing through the platinum. This may be held as excluding the passage of *carbonic oxide, marsh-gas,* and *olefiant gas,* all represented in the coal-gas.

Hydrosulphuric acid.—This gas, prepared from sulphide of antimony and hydrochloric

acid, washed, and dried over chloride of calcium, was then circulated through the outer porcelain tube. The hydrosulphuric acid was nearly all decomposed into sulphur and hydrogen, the latter coming through the platinum at the rate of 9 cub. centims. in five minutes. A trace of hydrosulphuric acid may also have passed through, as the mercury of SPRENGEL's tube was slightly soiled; but no indication of this gas could be perceived in the hydrogen collected. It, appears, then, that hydrosulphuric acid is to be classed among the non-penetrating gases. The result appears to be:—

I. Gas capable of passing through a septum of platinum 1·1 millim. in thickness at a full red heat.

Hydrogen (211 cub. centims. per hour).

II. Gases incapable of passing through a septum of fused platinum 1·1 millim. in thickness at a full red heat.

Oxygen	. (not to the extent of 0·2 cub. centim. per hour.)	
Nitrogen	,,	,,
Chlorine	,,	,,
Hydrochloric acid .	,,	,,
Vapour of water .	,,	,,
Carbonic acid . .	,,	,,
Carbonic oxide . .	,,	,,
Marsh gas (C H$_4$) .	,,	,,
Olefiant gas . . .	,,	,,
Hydrosulphuric acid	,,	,,
Ammonia . . .	,,	,,

It remains to be discovered whether a sensible passage of any of these gases could be effected through a platinum septum much reduced in thickness, or through the same septum under the influence of a considerably higher temperature. A fallacious appearance of permeation is sometimes occasioned by the escape from the platinum itself of a small quantity of gas, particularly of carbonic oxide and hydrogen, as will immediately appear. The permeation is in consequence never unequivocal for the first hour or two that the platinum septum is heated.

One of the curious experiments of M. DEVILLE was repeated, in which hydrogen appears to escape from the platinum tube pretty much as the same gas would escape from a graphite diffusiometer—the platinum tube being full of hydrogen, while the annular space between the platinum and outer porcelain tube was occupied by atmospheric air. At the maximum temperature the supply of hydrogen to the platinum tube was shut off, as that gas entered at one end of the tube, while the other end of the platinum tube was left in connexion with a barometer-tube dipping into a cistern of mercury. Immediately the mercury began to rise in the gauge tube from the passage of

hydrogen outwards through the walls of the platinum tube; and the latter in the end became nearly vacuous from the complete escape of the hydrogen.

Heated platinum tube containing hydrogen; air outside.

Time.	Rise of mercury in gauge barometer.
0 minute.	0 millim.
10 minutes.	115 millims.
20 ,,	245 ,,
30 ,,	400 ,,
40 ,,	535 ,,
50 ,,	645 ,,
60 ,,	710 ,,

the actual height of the atmospheric barometer being 750 millims. at the same time. The tension of the residual gas was therefore no more than 40 millims. of mercury. The ratio between the volume of gas at the beginning and end of the hour is here as 18·75 to 1; whereas in a diffusion experiment of hydrogen into air, the ratio would be as 3·8 to 1. Further, the residual gas in the platinum tube still retained a small portion of hydrogen. Withdrawn by means of the Sprengel pump and examined, the residual gas in the platinum tube amounted to 3·56 cub. centims., and consisted of

Nitrogen	3·22 cub. centims.
Hydrogen	0·34 ,,
	3·56 ,,

The available capacity of the platinum tube was 113·1 cub. centims.; and when the tube was heated, the gas driven out by dilatation measured in the cold 39·5 cub. centims., leaving in the hot platinum tube 73·6 cub. centims. of gas estimated at 20° C. and barom. 760 millims. It was found necessary in these experiments to stuff that portion of the platinum tube that was placed across the furnace and strongly heated, with asbestos, to give support to the tube when softened by the heat of ignition, and to prevent the tube from collapsing.
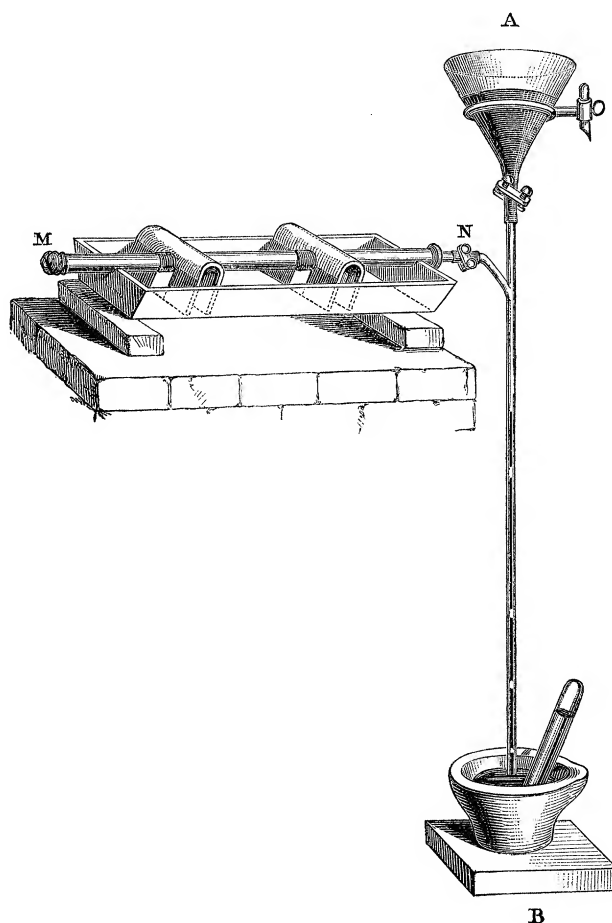
It is difficult to say where the small volume of nitrogen found in the platinum tube, amounting to 3·22 cub. centims., actually came from. It appears too great in amount to have formed an impurity in the original hydrogen gas, or to have gained access to the vacuum through defective joinings in the apparatus. Its presence suggests the inquiry, admitting that nitrogen cannot pass alone through platinum into a vacuum, whether the same gas may not be enabled to pass, in some small proportion, while hydrogen is simultaneously travelling through the platinum in the opposite direction. The liquid or the gaseous hydrogen occupying the platinum septum would thus form a vehicle or channel, by the help of which another analogous body like nitrogen might be conceived capable of passing through the platinum in small quantity, by a process of liquid or gaseous diffusion.

Absorption and detention of Hydrogen by Platinum.—The passage of a gas through a colloid septum is preceded by the condensation of the gas in the substance of the septum, according to the views taken in this paper.   Is a plate of ignited platinum capable, then, of condensing and liquefying hydrogen gas? The subject could scarcely admit of experimental investigation without the application of the same useful air-exhauster that was employed with the non-metallic colloids. The metal was always treated in the same manner; so that a description of the details of one experiment will apply to all*.

Platinum wire or plate being provided, the surface of the metal was first divested of all adhering oily matter, by boiling in caustic alkali and afterwards in distilled water.

The platinum, generally in the form of wire, was then introduced into a porcelain tube M, N (fig. 2), glazed both outside and inside, 0·55 metre in length and 23 millims.

Fig. 2.

in internal diameter. This tube could be heated either by means of the combustion-furnace used for organic analysis, or by placing the tube across the chamber of a small

* Platinum in the peculiar condition of platinum-black absorbs 745 times its volume of hydrogen gas.—Traité de Chimie Génerale, par MM. PELOUZE et FRÉMY, t. iii. p. 398.

cylindrical furnace.   The porcelain tube was fitted at both ends with perforated corks, well cemented with fused gutta percha, and provided each with a small quill tube.   Such may be described as the distillatory apparatus employed.   It was connected at the end N with the Sprengel pump A B, to be used as an exhauster and transferrer of gas, by means of good caoutchouc adapters (not vulcanized), and at the other end, M, with the apparatus for supplying dry hydrogen, atmospheric air, or any other gas.   By a screw clamp upon the adapter at M, the tube could be closed, and the gas-producing apparatus then detached, leaving the porcelain tube shut at one end.   A tube of the hard glass used in combustion analysis, may be substituted for the porcelain tube in many such experiments.   A less degree of heat suffices than was at first supposed.

The porcelain tube is exhausted by continuing the action of the Sprengel for ten or fifteen minutes, till small bubbles of gas cease to be delivered by the tube A B in the mercurial trough below.   The sufficiency of the joints is thus first ascertained.   Heat being then applied to the porcelain tube, its impermeability at a red heat will also be tested.

The platinum, when introduced, was confined to about two-thirds of the central portion of the porcelain tube, which could be conveniently heated.   The apparatus obviously affords the means both of heating the platinum in a vacuum and also in an atmosphere of hydrogen or any other gas admitted into the interior of the porcelain tube at M.

Fused platinum.—Articles of manufactured platinum appear now to be prepared exclusively from the fused metal.

1. A quantity of clean platinum wire from fused metal, measuring 0·695 metre in length, 4·1 millims. in diameter and 201 grms. in weight, was bent and introduced into the porcelain tube, which was then exhausted.   The platinum was first heated alone for an hour to drive off any natural gaseous product, and then dry hydrogen gas was admitted to the porcelain tube, the gas being evolved from pure sulphuric acid and pure zinc.   The hydrogen was conveyed in excess into the porcelain tube, at a cherry-red heat, and the temperature was then allowed to fall in a gradual manner—a procedure which was found to promote the absorption of the gas.   The platinum was thus retained for about twenty minutes in an atmosphere of hydrogen, at a temperature partly above and partly below dull redness, terminating with the lower temperature. After the fire was withdrawn and the tube allowed to cool, air or nitrogen was driven through it, and all free hydrogen thus expelled from the apparatus.

The closed tube was now exhausted in the cold, but no hydrogen came off.   The platinum being still retained in a good vacuum, heat was again very gradually applied, and the action of the Sprengel pump maintained.   Simultaneously with the first appearance of visible ignition, gas began to be evolved.   In one hour, the porcelain tube being heated to redness, 2·12 cub. centims. of gas were collected, of which about one-third was collected in the first ten minutes.   It was found, by explosion with oxygen, to consist of—

$$\text{Hydrogen} \quad . \quad . \quad . \quad . \quad . \quad 1\cdot93 \text{ cub. centim.}$$
$$\text{Nitrogen} \quad . \quad . \quad . \quad . \quad . \quad 0\cdot19 \qquad ,,$$

Now, taking the specific gravity of the platinum wire at 21·5, the volume of 201 grms. of metal will be 9·34 cub. centims. Hence one volume of platinum held, the gas being measured cold,

$$0\cdot207 \text{ vol. hydrogen.}$$

The platinum did not appear sensibly altered in lustre, or in any other way, by its relation to the hydrogen.

2. The same piece of platinum wire was drawn out into four times its first length, and the experiment of charging with hydrogen was repeated. The platinum gave up at a red heat, maintained for one hour, 1·8 cub. centim. of gas, of which 1·6 cub. centim. was hydrogen. Here one volume of platinum appears to have held

$$0\cdot171 \text{ vol. hydrogen.}$$

The absorption of hydrogen has not been increased by increasing the surface of the metal.

In two further experiments upon the same platinum wire, the volume of hydrogen retained by one volume of platinum was—

3.   0·173 cub. centim. hydrogen.
4.   0·128   ,,   ,,

There is an evident tendency of the hydrogen taken up to diminish in quantity. These experiments have the advantage for comparison with the earlier observations on the penetration of a platinum septum by hydrogen gas, that both wire and tube had been drawn out from the same mass of fused metal. No iridium had been added to this platinum, as is sometimes done to increase the elasticity of the metal. The absorption of hydrogen is small, amounting, according to the mean of the four observations, to 17 per cent. of the volume of the platinum. At the temperature of a low red heat, when the absorption took place, the gas would be considerably dilated, to the extent of at least three times its volume stated above, or to about 51 per cent., half the volume of the platinum. It is to be considered whether an absorption of half a volume of gas would be sufficient to account for the observed penetration of a septum of metal 1·1 millim. in thickness. The data appear to favour an affirmative conclusion; but their value cannot be very decidedly estimated.

It appears necessary to recognize in platinum a new property, a power to absorb hydrogen at a red heat, and to retain that gas at a temperature under redness for an indefinite time. It may be allowable to speak of this as a power to occlude (to shut up) hydrogen, and the result as the *occlusion* of hydrogen by platinum.

The observation was extended to platinum in other conditions of form, but where, it is to be observed, the metal had not been fused, but only welded, and was not of recent manufacture.

5. Of the grey pulverulent spongy platinum, prepared from the ammonio-chloride,

22·2 grms. were heated by the combustion-furnace, and for half an hour allowed to cool gradually in dry hydrogen gas, as in the preceding experiments. The volume of the platinum is 1·032 cub. centim. by calculation. In the first experiment it yielded to heat and the action of the Sprengel pump 2·2 cub. centims. of a gas which burned like hydrogen. In a second experiment the platinum yielded in one hour (when it appeared to be exhausted) 1·7 cub. centim. of gas, found by explosion to consist of hydrogen 1·52 cub. centim., and nitrogen 0·18 cub. centim. Here one volume of spongy platinum appears capable of occluding

<div align="center">1·48 vol. hydrogen.</div>

6. Wrought platinum, in the form of plate from an old crucible cut up, after washing and ignition, was charged with hydrogen three times in succession. The weight of the platinum was 24·1 grms., and its volume 1·12 cub. centim. It yielded in seventy-five minutes 4·19 cub. centims. of gas, and in thirty minutes further 1·5 cub. centim. more, making together 5·69 cub. centims., of which 4·94 cub. centims. proved to be hydrogen; therm. 14°·2, barom. 760 millims. Not a trace of carbonic acid was found in the gas before or after explosion. Again, after a second charge, 5·12 cub. centims. of gas were given up in an hour, of which 4·4 were hydrogen; and lastly, 3·76 cub. centims. in an hour, of which 3·42 were hydrogen. Hence, occluded by 1 vol. wrought platinum—

<div align="center">
5·53 vols. hydrogen.

4·93 „   „

3·83 „   „
</div>

The volume of occluded hydrogen is much larger than in the fused platinum, or even in the spongy platinum. It exhibits a tendency to fall off on repeating the experiment. The declension in absorbing-power may possibly be connected with the reduced duration of the exposure to hydrogen of the metal while cooling.

7. Wrought platinum, which had been formed many years ago into a small tube, weighing 64·8 grms., 0·322 metre in length and 5 millims. in diameter, was cut into three equal lengths for convenience in placing the metal within the porcelain tube, to be heated and charged with dry hydrogen. By an hour's exhaustion afterwards the platinum yielded 9·2 cub. centims. gas, of which 8·9 were hydrogen. The volume of the platinum itself was 3·9 cub. centims.; and one volume of metal had therefore occluded 2·28 vols. hydrogen, measured at about 20° C. In all such experiments, besides blowing out the free hydrogen by air, the apparatus was also thoroughly exhausted by the Sprengel pump in the cold, before the occluded hydrogen was extracted.

The lustre and appearance of the metallic platinum was not altered by the ingress of the hydrogen; but after the escape of the gas the platinum appeared whiter in colour, and the surface was covered by minute blisters.

Repeating the experiment, the gas collected by an hour's exhaustion was 8·7 cub. centims., of which 8·46 cub. centims. were hydrogen. Here the metal occluded 2·8 vols. of hydrogen.

The same platinum was a third time charged with hydrogen; but on this occasion the platinum was placed in a tube of hard glass, and the tube connected with the air-exhauster. The glass tube was heated by an oil-bath, and the platinum kept *in vacuo* at a temperature of 220° C. for an hour. Not a bubble of gas was evolved. The glass tube was afterwards heated by a small Bunsen burner, which was calculated to give a degree of heat little short of visible redness, still no hydrogen came off. The tube was now heated sufficiently to soften glass (500°). Gas began to come off, of which 1·8 cub. centim., containing 1·72 hydrogen, were collected in ten minutes. The glass tube having cracked, the whole apparatus was allowed to cool, and the platinum transferred to a porcelain tube. Further heated by a combustion-furnace for one hour, the platinum gave off 8·6 cub. centims. gas, of which 8·2 were hydrogen. The platinum therefore appears to have occluded altogether 3·79 vols. of hydrogen.

The preceding experiment appeared to show a complete sealing up of the occluded hydrogen at low temperatures, seeing that, although nearly four volumes of gas were present, none escaped below a red heat. But to test the effect of time at the temperature of the atmosphere, the platinum, again charged with hydrogen, was sealed up hermetically in a glass tube, which it nearly filled, and not opened for two months. The air in the tube was was then transferred and examined. It did not exhibit any reduction of volume under the electric spark or a pellet of spongy platinum. The air therefore appeared to contain no hydrogen; the latter had not diffused out, but, it is to be presumed, was retained by the platinum without loss. These experiments, although related last, were the first performed in this inquiry. The included hydrogen was never entirely extracted in an hour, and is probably understated. The gas always came off gradually, more than one half of the whole in the first twenty or thirty minutes. The last results may be stated as follows:—

1 vol. hammered platinum occluded 2·28 vols. hydrogen.
    „   „   „   2·80   „
    „   „   „   3·79   „

The high absorbing power of the hammered platinum, or rather the low absorbing power of the fused metal, was ascribed to a mechanical difference between the two—to a more open texture in the former, permitting more free access of hydrogen, liquefied as it may be, to the interior of the metal.

8. The extrication of occluded hydrogen from platinum had always required a degree of temperature verging upon a red heat, even when aided by a vacuum; and this remains true of hydrogen originally absorbed at or near a red heat. But the fact appears to be compatible with the absorption of the gas, under the pressure of the atmosphere, at a considerably lower temperature. Thin platinum-foil was first deprived of a little natural gas by ignition *in vacuo* in the porcelain tube. The foil was afterwards placed in a glass tube and heated again in a stream of hydrogen, to a temperature not exceeding 230° C., for three hours, by means of an oil-bath, and further allowed to cool slowly in an atmo-

sphere of the same gas for several hours. A second glass tube receiver, to which the platinum-foil was transferred, was exhausted, as usual, at 20° C. without any sensible evolution of gas. With a red heat superadded, gas came off in twenty minutes (but nearly all in the first seven minutes) to the extent of 0·75 cub. centim., of which 0·56 cub. centim. proved to be hydrogen. The volume of 8·3 grms. of platinum is 0·385 cub. centim. Hence one volume of platinum foil appears to take up, in three hours,

<div align="center">1·45 vol. hydrogen at 230° C.</div>

9. The same portion of platinum-foil was again charged with hydrogen at a still lower temperature, namely between 97° and 100°, for three hours. Submitted to exhaustion at red heat, the platinum now gave off 0·5 cub. centim. of gas in thirty-five minutes, of which about 0·3 cub. centim. were hydrogen. One volume of platinum-foil has taken up

<div align="center">0·76 vol. hydrogen at 100°.</div>

By this property platinum is connected with palladium, which of all metals appears to possess the power of absorbing hydrogen in the highest degree.

<div align="center">*Palladium.*</div>

Of late years palladium has become comparatively uncommon; and some difficulty was experienced at first in procuring more than a gramme or two of the metal, in the form of thin foil. The palladium-foil first employed weighed 1·58 grm., and measured 0·133 cub. centim., taking the specific gravity of the metal at 11·86, and had a surface of 0·00902 square metre. It gave off, when heated *in vacuo* for one hour, 1·50 cub. centim. of natural gas, containing no compound of carbon, but consisting of hydrogen and air.

1. As it appeared from preliminary experiments that the occlusion of hydrogen by palladium was likely to be a phenomenon exhibited at a comparatively low range of temperature, the metal was heated in hydrogen no higher than 245° C., by an oil-bath, and allowed to cool very slowly, so as to pass through still lower ranges of temperature which might be favourable to the absorption of hydrogen. The metal, when afterwards transferred to the distillatory glass tube, appeared to give out nothing to a vacuum at 17°·8 C. and barom. 759 millims. But the moment the combustion-furnace was lighted under the tube, gas come off most freely. Of the first portion collected, 11·77 cub. centims. contained 11·74 cub. centims. hydrogen. The gas ceased to be evolved in fifteen minutes, when 69·92 cub. centims. were collected, of which the greater part came over in the first ten minutes. Hence palladium has taken up a large volume of gas when the temperature of the metal never exceeded 245° C.

<div align="center">1 vol. palladium held 526 vols. hydrogen.</div>

2. In a similar experiment the temperature of absorption was still further lowered with good effect. The palladium was exposed to hydrogen between 90° and 97° C. for three hours, and then allowed to cool in the gas for one hour and a half. Now placed in a glass tube, exhausted, and heated by a gas-flame, the palladium gave off gas in a

continuous stream for twelve minutes, when it ceased. The gas amounted to 85·56 cub. centims., of which 96·8 per cent. was hydrogen; therm. 17°·5, barom. 764 millims.

<div style="text-align:center">1 vol. palladium held 643·3 vols. hydrogen.</div>

By the care of my zealous assistant, Mr. W. C. ROBERTS, the hydrogen employed in these experiments was purified to the highest degree by passing it in succession through alcohol, water, caustic potash, and tubes of 0·7 metre each, filled with broken glass impregnated with nitrate of lead, sulphate of silver, and oil of vitriol. The gas was inodorous, and burned with a barely visible flame.

No alteration was sensible in the metallic appearance of the palladium-foil when charged with hydrogen, or when discharged. The foil was much crumpled and rather friable after repeated use; but this may have arisen from frequent handling.

3. Palladium appears to absorb hydrogen largely, even at natural temperatures, provided that the metal has been recently ignited *in vacuo*. The foil, without such preparation, was placed in a bottle of pure hydrogen for several hours, but yielded nothing when afterwards ignited in the Sprengel vacuum. The foil, however, being immediately returned after cooling to a stoppered bottle containing hydrogen, and left in the gas for a night, absorption now took place—air rushing in, on opening the stopper, as into a partial vacuum; therm. 19°. When the palladium-foil was afterwards transferred to a glass tube and connected with the Sprengel pump, it was found difficult to obtain a vacuum for some time, owing to hydrogen coming off at the temperature of the atmosphere. But after a fair vacuum was produced 6·96 cub. centims. were collected, of which 6·78 proved to be hydrogen. Heat was then applied, and 42 cub. centims. came over in five minutes, making altogether more than 50 cub. centims., or 376 volumes of gas. The absorption of hydrogen appears, then, to be suspended at a low temperature, unless the condition of the metal be favourable. The action of a plate of clean platinum in determining the combustion of explosive gas is equally critical at a low temperature.

4. A different specimen of palladium-foil, weighing 5·76 grms., and having a volume of 0·485 cub. centim., was charged with hydrogen, and discharged, more than once. In the second experiment, the foil was heated in hydrogen at 100° for three hours. Distilled afterwards in a porcelain tube at a low red heat in the usual way, the palladium was found to have absorbed, at 100°,

<div style="text-align:center">347·7 vols. of hydrogen measured at 18°·2 C. and barom. 756 millims.</div>

5. So large an absorption of hydrogen should increase the weight of the palladium sensibly, notwithstanding the lightness of the gas. One litre, or 1000 cub. centims., of hydrogen at 0° C. and 760 millims. weighs 0·0896 grm. Of new palladium-foil, believed to be from *fused* metal, 5·9516 grms. increased to 5·9542, or by 0·0026 grm., when the metal was charged with hydrogen at 100° for four hours. This amounts to only 29·01 cub. centims. of hydrogen at 0° C. and 760 millims. barom. The gas actually extracted afterwards from the palladium did not exceed 34·2 cub. centims. at 19° C., and barom. 758 millims., equivalent to 31·84 cub. centims. at 0° C. and 760 millims.

barom. The whole gas extricated (68 vols.) seems unusually small, but it corresponds closely enough with the volume calculated from the increase of the palladium in weight. An inferior absorbing power for hydrogen appears to be connected in both platinum and palladium with the fusion of the metal.

6. A portion of similar palladium-foil, charged with hydrogen, was found to have its gas reduced from 20·7 to 16·2 cub. centims. after exposure to the air for forty-two hours. The liquid hydrogen, whether held by the substance or in the pores of the metal, appears therefore to evaporate slowly at the temperature of the atmosphere, therm. 19°, barom. 752 millims.

7. Spongy palladium, from the ignition of the cyanide, being heated in hydrogen at 200°, and allowed to cool slowly in the same gas for four hours, the metal was found to have taken up 686 vols. of hydrogen.

Treated in a similar manner with air, spongy palladium exhibited no absorbing-power for oxygen or nitrogen.

Hydrogen, condensed either in the palladium sponge or foil, was observed to have its chemical affinities enhanced. The palladium being placed in dilute solutions of the following substances for twenty-four hours in the dark at the ordinary temperature, the action of the hydrogen became manifest.

Persalt of iron became protosalt.

Ferricyanide of potassium became ferrocyanide.

Chlorine-water became hydrochloric acid.

Iodine-water became hydriodic acid*.

Apart from hydrogen, the palladium sponge exhibits a power of selection and absorption of alcohol in preference to water. 30 grms. of the sponge were left in contact with 9·5 cub. centims. of dilute alcohol of specific gravity 0·893, for fifty-one hours, sealed in a tube. The supernatant liquid now drawn off to the extent of 3·9 cub. centims. was of specific gravity 0·901, while the portion retained by the palladium was found when distilled to be of specific gravity 0·885, or it was sensibly concentrated. This chemical action of palladium sponge was more than once verified. Platinum sponge, on the other hand, exhibited no indication of a similar separating-power; nor did the sponge of iron reduced by hydrogen from the oxide.

8. Connected, it may be, with this chemico-molecular action of palladium is the variable absorptive power for different liquids exhibited by palladium-foil. Immersed in various liquids for an hour, and afterwards dried by pressure for a few seconds between folds of blotting-paper, a quantity of palladium-foil represented by 1000 was found to retain in its pores—

<div align="center">

Of Water . . . . 1·18 part.

Of Alcohol (0·802) . . . . . 5·5 parts.

</div>

---

* The power of platinum-black charged with hydrogen to communicate the latter element to organic compounds has lately been observed by M. P. DE WILDE, following Dr. DEBUS.—Bulletin de la Société Chimique, Mars 1866.

Of Ether . . . . 1·7 part.
Of Acetone (0·794) . . . . . 0·54 „
Of Glycerine . . . . 4·5 parts.
Of Benzol . . . . 3·5 „
Of Oil of sweet almonds . . . 18·1 „
Of Castor-oil . . . . 10·2 „

The superior penetrativeness of alcohol over water is well marked; capillary action appears to merge into a chemical affinity. Liquid hydrogen would also appear as highly absorbable by palladium-foil. It would appear also to be separable from other gases (or liquids), as alcohol is from water, by the palladium-pores.

Alloy of 5 palladium and 4 silver.—The power to absorb hydrogen appears to extend to this alloy of palladium. A plate of the alloy, about 180 millims. in length, 31 millims. in width, and weighing 74·3 grms., was bent. so as to be able to enter a wide porcelain tube that could be exhausted of air when required. The volume of the palladium alloy was 6·21 cub. centims. The plate of metal being placed in the porcelain tube, had hydrogen gas passed over it at a low red heat for one hour, and was then allowed to cool slowly in the same gas. Taken out and examined, the metal was not visibly altered. For the extrication of gas the metal was distilled in the porcelain tube heated by jets of gas, and connected with the Sprengel pump, as usual. In seven minutes after the gas-furnace was lit, 24 cub. centims. of gas came off; in ten minutes more, 80·71 cub. centims.; and in seventy-five minutes more, 36·75 cub. centims., making altogether 141·46 cub. centims. Of this gas 127·74 cub. centims. proved to be hydrogen, the remainder being nitrogen, derived, no doubt, from the large imperfectly exhausted porcelain tube. The palladium alloy, in the form of a thick plate, appears therefore to have held

20·5 vols. hydrogen, measured at 18°·2 and barom. 756 millims.

This alloy of palladium becomes crystalline by heating, and appears to lose much of its absorbent power at the same time.

The conclusion, then, is that welded palladium, in the condition of thin foil, readily absorbs hydrogen, to the extent of upwards of 600 times the volume of the metal at a temperature under the boiling-point of water, upwards of 500 volumes at 245°, and less at higher temperatures, the metal being always surrounded by hydrogen under atmospheric pressure. Hydrogen is also largely absorbed, although less constantly, at ordinary temperatures. On the other hand, palladium already fully charged with hydrogen at or under 100°, and under the pressure of the atmosphere, begins to give out gas when exposed either to atmospheric air or to a vacuum at the original temperature of absorption; and the gas is freely discharged at 200° C.

It is probable that hydrogen enters palladium in the physical condition of liquid, whether the phenomenon proves to be analogous to the imbibition of ether, chloroform, and such solvents by the colloid india-rubber, or whether a certain porosity of structure in the palladium is required. The porosity of the metal is supposed to be of that high

degree which will admit liquid but not gaseous molecules. Now the numerous liquid compounds of carbon and hydrogen have all a nearly similar density, generally a little under that of water. There is no reason to suppose that the density of liquid hydrogen would differ greatly from the hydrocarbon class; but then the surprising lightness of hydrogen gas must cause liquid hydrogen to yield a volume of vapour disproportionately large when compared with the former class of substances, or, indeed, with any other substance whatever. The absorption of hydrogen by palladium will appear, then, less extravagantly great when viewed as the absorption of a highly volatile liquid capable of yielding an exceedingly light vapour, rather than that of a gas.

An excellent opportunity of observing the penetration by hydrogen of a compact plate of palladium, 1 millim. in thickness, was afforded by a tube of that metal constructed by Mr. MATTHEY. This tube was said to have been welded from palladium near the point of fusion of the metal. The length of the tube was 115 millims., its internal diameter 12 millims., thickness 1 millim., and external surface 0·0053 of a square metre. It was closed by thick plates of platinum soldered at both ends, one of the plates being perforated by a long small tube of platinum, by which the cavity of the palladium tube could be exhausted of air.

Now the closed palladium tube remained air-tight, when exhausted by the Sprengel tube, at the ordinary temperature, at 260°, and at a temperature verging on low redness, the gas without being atmospheric air. Hydrogen being then substituted as the external gas, the walls of the palladium tube still remained impermeable at a low temperature. No hydrogen gained the interior in three hours at 100°. But the temperature being gradually raised by means of an oil-bath to 240°, hydrogen then began to come through, and at a gradually increasing rate to 265°. The hydrogen then entered steadily at the rate of 8·67 cub. centims. in five minutes. This gives a rate of 327 cub. centims. for a square metre of surface per minute. Heated to a temperature just short of redness, the passage of hydrogen was increased to 11·2 cub. centims. in five minutes, or 423 cub. centims. for a square metre per minute.

With coal-gas as the external atmosphere the penetration of the palladium began about the same temperature, and was continued at 270° at the rate of 57 cub. centims. for a square metre of surface per minute. The penetrating gas had no odour of coal-gas, contained no trace of carbon, and appeared to be absolutely pure hydrogen. The exact isolation of the latter gas by septa of both platinum and palladium appears most extraordinary.

A quantitative determination of the hydrogen in a gaseous mixture could probably be effected by means of the hollow cylinder of palladium.

Is the power to penetrate the metals in question confined to hydrogen? It has been lately concluded by Dr. C. WETHERILL that the turgescence of the ammonium amalgam depends entirely upon the retention of hydrogen gas-bubbles[*]; hydrogen, then, appears to exhibit an attraction of a peculiar kind for mercury. The ready liquefaction of the same gas by the platinum metals evinces also a powerful mutual attraction. The only

* American Journal of Science, vol. xlii. No. 124.

other volatile body which has been observed to pass, like hydrogen, through a plate of palladium is common ether—and that at the atmospheric temperature, while a passage was denied to hydrogen at the same time. The palladium was in the form of foil. Although thin foil of this metal is generally visibly porous and allows air to pass through like a sieve, a tube diffusiometer, covered with a disk of the selected palladium foil, and standing over mercury, retained a volume of 40·5 millims. of air over a vertical column of 155 millims. of mercury for twenty-four hours without depression of the mercury. The air was dried by sticks of potash, but still it did not penetrate the palladium. Dry hydrogen was then conducted to the upper surface of the palladium disk, but still without any penetration by that gas after several hours. Cotton-wool moistened with ether was now placed upon the disk, when, after eight minutes, the confined air within the tube began to expand; and in the course of an hour longer, the 40·5 volumes of confined air increased to 90·4 (thermometer 18°·5, barometer 758), when the expansion ceased. The increase of volume appeared to be due entirely to ether-vapour, absorbable by a pellet charged with sulphuric acid. Why hydrogen proved to be incapable of penetrating the palladium in such circumstances it is difficult to say. It can only be imagined that the palladium foil may have previously condensed on its surface a minute film of foreign matter, which rendered the palladium inactive to hydrogen but not to ether-vapour.

On the other hand, the penetrating power of hydrogen, here referred to the liquefaction of that gas, appears not to be solely confined to metallic septa. There is reason to suspect that in diffusing through a plate of graphite hydrogen passes in a small proportion as a liquid, without any counterdiffusion of air. Hence the constant excess observed of the diffusive coefficient of hydrogen, which came out 3·876, 3·993, and 4·067 *, instead of the theoretical number 3·8, corresponding to the density of the gas referred to air. Such phenomena of gaseous penetration suggest a progression in the degree of porosity. There appear to be (1) pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals, (2) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion, as in artificial graphite, and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite.

Osmium-iridium.

A portion of small grains of osmium-iridium, amounting to 2·528 grms., was exposed to hydrogen through all descending temperatures from a red heat, as the preceding metals had been treated. The osmium-iridium was then heated again to redness in the Sprengel vacuum, to extricate any hydrogen that might have been absorbed. But only a bubble or two of gas, too minute to be measured, passed over in fifteen minutes, at a red heat. Osmium-iridium, then, exhibits no absorbent power for hydrogen—a result which is consistent with the crystalline character of the substance.

* Philosophical Transactions, 1863, p. 404.

Copper.

The power to occlude gases appears not to be confined to palladium and platinum among the metals. The exact experiments of M. DUMAS, by which the atomic weights of the leading elements were definitely settled, afford an indication of the absorption of hydrogen gas by spongy metallic copper reduced from the oxide, sufficient to affect the weight of the metal to the extent of about 3 parts in 100,000 *.

1. With the view of applying the method of extracting gas followed in the treatment of the preceding metals, so much oxide of copper was reduced by hydrogen as was calculated to yield 50 grms. of metallic copper. The reduced metal was again heated to redness and slowly cooled in a stream of dry hydrogen. After free exposure to the air for a few minutes, the metal was now submitted, at a red heat, to the action of the Sprengel pump. It then gave off in one hour 3·35 cub. centims. of gas, measured cold, which appeared to be pure hydrogen (the explosion with oxygen indicated 3·4 hydrogen). Taking the specific gravity of copper at 8·85, 50 grms. of that metal would be 5·65 cub. centims. in volume, and the result is that

1 vol. reduced copper sponge occludes 0·6 vol. hydrogen.

Hydrogen being about 12,000 times as light as copper (at 15°), 1 part of gas by weight has been taken up by 20,000 parts of metal.

2. The same weight and volume of fine copper, in the form of wire, thoroughly cleaned, was exposed to hydrogen at a red heat, and then submitted to exhaustion for one hour. It gave 2·6 cub. centims. gas, of which 2 cub. centims. were hydrogen, and the remaining 0·6 principally carbonic oxide. It may be represented that

1 vol. wrought copper occludes 0·306 vol. hydrogen.

Where a metal, such as wrought copper, may contain small quantities of carbon and oxygen, an obvious cause will exist for the production and evolution of carbonic oxide under the influence of heat. Gas so generated appears to be added to the occluded hydrogen when extricated, in the last experiment.

Gold.

1. A quantity of gold was precipitated from the assay cornettes used below by means of oxalic acid. The gold weighed 93·3 grms., with a volume of 4·83 cub. centims., taking the specific gravity of the metal as 19·31. Exhausted at a red heat without any further treatment, the reduced gold yielded 3·4 cub. centims. of gas, which may therefore be supposed to be gas usually present in gold reduced in the manner described. This is 0·704 vol. of the gold. The occluded gas in precipitated gold gave to analysis

---

* Annales de Chimie et de Physique, 3 sér. t. viii. p. 205. The observations of M. MELSENS show that 240 grms. of copper may fix about 0·007 grm. of hydrogen, most being fixed when the oxide of copper is reduced by hydrogen at a low temperature. In the subsequent oxidation of the copper the gas does not come out suddenly, but in a gradual manner.

0·05 cub. centim. Oxygen.

1·50 „   „   Carbonic acid.

1·85 „   „   Carbonic oxide, &c.

3·40

2. Of the original cornettes of fine gold, from gold assays conducted several months before, 93·3 grms., having a volume of 4·83 cub. centims., were submitted without any further treatment to aspiration at a red heat. The gold gave up in the first half hour 9·45 cub. centims. of gas, and in the second half hour 0·8 cub. centim., making together 10·25 cub. centims. Hence 1 volume of the gold cornettes appears to hold 2·12 volumes of gas. This gas consisted of

6·70 cub. centims. Carbonic oxide.

1·50 „   „   Carbonic acid.

1·58 „   „   Hydrogen.

0·44 „   „   Nitrogen.

0·03 „   „   loss.

10·25

The cornettes do not appear ever to assume again so much gas as they first acquired in the assay muffle. It follows that the weight of a gold cornette is increased about 2 parts in 10,000 by the weight of occluded gas. As the gold also retains 7 or 8 parts of silver in 10,000, it follows that the absolute quantity of gold in a cornette is less than the weight of the cornette as indicated by the balance, by 1 part in 1000. This does not disprove the accuracy of the usual gold assay, which is always made in comparison with gold of known composition as a check, and is therefore *relatively* true.

3. The same volume of gold cornettes, amounting to 4·83 cub. centims., heated again in carbonic oxide gas, gave up afterwards 1·6 cub. centim. of occluded gas, composed of

1·4 cub. centim. Carbonic oxide.

0·2 „   „   Carbonic acid.

1·6

4. The same mass of gold cornettes heated in hydrogen gas, gave up afterwards in one hour 2·7 cub. centims. of gas, which appeared to consist of

2·34 cub. centims. Hydrogen.

0·36 „   „   Nitrogen, &c.

2·70

The power of this metal to occlude hydrogen gas is very sensible. The metal here appears to hold 0·48 volume of hydrogen gas. The same gold, when dissolved and precipitated, was also found capable of holding 0·44 volume of hydrogen.

5. The same mass of cornettes, heated in carbonic acid gas, gave up afterwards in one hour 1·05 cub. centim. gas, in which baryta-water showed the presence of

0·78 cub. centim. Carbonic acid.

The charged cornettes were always freely exposed to air for some time before occluded gas was extracted from them and measured, so as to allow the escape of any loosely attached gas.

6. The same cornettes were heated and cooled in a stream of dry air, in like manner as they had been treated with other gases. The occluded air given out in one hour amounted in two different experiments to 1·15 and 0·95 cub. centim. respectively. The gas of the second experiment gave

$$
\begin{array}{lll}
0\text{·}82 \text{ cub. centim. Nitrogen} & . = & 86\text{·}3 \\
0\text{·}08 \quad ,, \qquad ,, \quad \text{Carbonic acid} = & 8\text{·}4 \\
0\text{·}05 \quad ,, \qquad ,, \quad \text{Oxygen} . \ . = & 5\text{·}3 \\
\overline{0\text{·}95} & & \overline{100\text{·}0}
\end{array}
$$

The whole occluded air amounts to 0·2 volume of the gold, and is principally *nitrogen*. The indifference of gold to oxygen is remarkable, and contrasts with the power of silver to occlude the same gas.

Silver.

1. Fine silver, in the form of wire, 2 millims. in diameter, with its surface duly purified, was first heated alone in the porcelain tube, and then exhausted of gas by the Sprengel tube in the usual way. The natural gas derived from this metal was small in quantity, and it appeared to come off almost entirely in one hour. The silver wire weighed 108·8 grms., and had a volume of 10·37 cub. centims., taking the specific gravity of pure silver as 10·49. The gas extracted amounted to

$$
\begin{array}{l}
2\text{·}2 \text{ cub. centims. in thirty minutes.} \\
\underline{0\text{·}8 \quad ,, \qquad ,, \qquad\qquad ,,} \\
3\text{·}0 \quad ,, \qquad ,, \quad \text{in one hour.}
\end{array}
$$

The gas consisted of

$$
\begin{array}{l}
2\text{·}4 \text{ cub. centims. Carbonic acid.} \\
\underline{0\text{·}6 \quad ,, \qquad ,, \quad \text{Carbonic oxide.}} \\
3\text{·}0
\end{array}
$$

Silver wire therefore appeared to hold occluded 0·289 volume of gas, principally carbonic acid. There is reason, however, to suppose that the occluded gas may really be oxygen, and that the latter was converted into carbonic acid at the temperature of extrication, by a trace of carbon existing in the fine silver.

2. The same quantity of silver wire was now charged with hydrogen, by being heated to redness and afterwards cooled slowly in that gas. The gas extricated amounted to

$$
\begin{array}{l}
2\text{·}3 \text{ cub. centims. in forty-five minutes.} \\
\underline{0\text{·}2 \quad ,, \qquad ,, \quad \text{in fifteen minutes.}} \\
2\text{·}5 \quad ,, \qquad ,, \quad \text{in one hour.}
\end{array}
$$

The gas consisted of

2·2 cub. centims. Hydrogen.

0·3 „ „ Nitrogen, &c.

2·5

The fine silver had therefore occluded 0·211 volume of hydrogen. The metal acquired a beautiful frosted appearance on the surface; and by repeated heating it became highly crystalline and brittle.

3. The same portion of silver was now charged with oxygen. The occluded gas given off amounted to

7·5 cub. centims. in thirty minutes.

0·3 „ „ „

7·8 „ „ in one hour.

The gas consisted of

7·6 cub. centims. Oxygen.

0·2 „ „ Nitrogen, &c.

7·8

The silver therefore held occluded 0·745 volume of oxygen. This gas, like the hydrogen in platinum, was permanently fixed in the metal at all temperatures below an incipient red heat. It did not tarnish the bright metallic surface of the silver, or produce any appearance suggestive of the oxidation of a metal.

4. The same portion of silver, after being dissolved in acid, precipitated as chloride, and reduced again, was exposed to atmospheric air at a red heat, and afterwards exhausted. The gas given off amounted to

5·56 cub. centims. in fifteen minutes.

0·30 „ „ „

5·86

Of this gas 5·56 cub. centims., or nearly the whole, proved to be oxygen gas; or the silver held occluded 0·545 volume of oxygen. This silver had been purified from the chloride, and it contained no trace of copper.

When silver, of British Standard (that is, containing 7·5 per cent. of copper), is exposed to air or oxygen at a low red heat, the silver becomes almost black on the surface from oxidation of the copper. Silver wire in this blackened state gave off several volumes of oxygen under the action of heat and a vacuum. Much of the superficial oxide disappeared at the same time. It appeared as if the operation tended to the reduction of the superficial oxide of copper, oxygen being liberated, and the copper absorbed by the mass of silver.

5. A specimen of silver reduced from the oxide, in the form of sponge, which was considered pure, but was not analyzed, occluded 6·15, 8·05, and 7·47 volumes of oxygen, in successive experiments, without any visible tarnish of the surface. Can the attraction

or affinity of silver for oxygen, which enables the pure metal to occlude that gas, be enhanced by the presence of a mere trace of some positive metal like copper?

6. The same specimen of fritted silver was found to occlude, in successive experiments,

0·907 vol. Hydrogen.

0·938 ,,   ,,

0·486 ,,   Carbonic acid.

0·545 ,,   ,,   ,,

0·156 ,,   Carbonic oxide.

Hydrogen and carbonic acid, as well as oxygen, appear to be taken up in larger proportion by this silver than by the former specimen of the same metal.

7. Of pure silver highly laminated, 500 leaves, weighing 12·5 grms., were exposed to air at a red heat, and thereafter exhausted at the same temperature. The silver (1 vol.) gave up 1·37 volume of oxygen, 0·20 volume of nitrogen, and 0·04 volume of carbonic acid.

It appears that silver has a relation to oxygen similar to that exhibited by platinum, palladium, and iron to hydrogen. The power of silver and of litharge in a state of fusion to absorb oxygen, and to allow that gas to escape on solidification, may be connected with the observed capacity of the colloid metal, softened by heat, to absorb the same gas, although to a less extent.

Iron.

The penetration of iron by hydrogen is demonstrated as clearly by MM. DEVILLE and TROOST as that of platinum. A thin tube of cast steel, 3 or 4 millims. in thickness, already enclosing hydrogen gas in its cavity, was surrounded by air or by nitrogen gas circulating in an annular space between the steel tube mentioned and a wider external porcelain tube. In the absence of any visible pores in the steel, hydrogen made its way through the substance of the metal, and escaped into the annular space as soon as the system of tubes was exposed to a red heat. A nearly if not entirely complete vacuum was formed within the iron tube*. In another modification of the experiment, carbonic oxide from an uncertain source appeared within the iron tube, particularly when the temperature was most elevated†.

Wrought iron, in the form of thin wire (No. 23), about 0·4 millim. in diameter, first carefully cleaned with caustic alkali and water, was heated alone in the porcelain tube exhausted of air, for the purpose of eliminating any natural gases.

1. Of the iron wire referred to, 46 grms., with a volume of 5·9 cub. centims., the specific gravity of the metal being taken at 7·8, were heated by the open combustion-furnace. Gas came off freely at a red heat,—

(1) In fifteen minutes, 15·6 cub. centims., containing 3·5 cub. centims. carbonic acid, or 22·4 per cent.

---

* Comptes Rendus, t. lvii. p. 965 (1863).   † Ib. t. lix. p. 102 (1864).

(2) In fifteen minutes, 7·17 cub. centims., containing 0·52 cub. centim. or 7·2 per cent. of carbonic acid. The gas of this and the following stages of observation now burnt with a blue flame, and was principally carbonic oxide.

(3) In thirty minutes, 10·4 cub. centims., of which 6·86 cub. centims. were carbonic oxide.

(4) In thirty minutes, 8·16 cub. centims., of which 0·12, or 1·4 per cent., was carbonic acid.

(5) In thirty minutes, 5·52 cub. centims., of which 0·03 was carbonic acid—that is, 0·5 per cent.

Hence 46 grms. of wrought iron have in two hours given off 46·85 cub. centims. of gas, measured at about 15° C.; or 1 volume of iron has discharged 7·94 volumes of gas, of which about two-thirds was carbonic oxide; and the metal does not appear to be yet quite exhausted. Iron is a metal not unlikely to contain small quantities of carbon and oxygen, both in chemical union with iron; and the gas extricated may partly be due to a reaction of these elements upon each other at a red heat.

2. In another similar experiment upon 32 grms. of clean iron wire (No. 21), measuring 4·1 cub. centims., the iron was heated in a small glass tube, to exclude the idea of the conceivable permeability of the porcelain tube. The iron gave off gas at a pretty uniform rate, which amounted in an hour to 29·8 cub. centims., of which 4·44 cub. centims. were carbonic acid, and the remainder principally carbonic oxide, with hydrogen and a trace of a hydro-carburet. Here the iron wire gave off 7·27 volumes of gas. .

3. In a third experiment on thin iron wire (No. 23), the extrication of the natural gases at a red heat was pushed to a greater degree of exhaustion. The weight of the iron was 39 grms., and its volume 5 cub. centims. In the first and second hour the gas collected was 45 cub. centims.; in the third hour 10·85 cub. centims.; in the fourth and fifth hours 5·65 cub. centims.; in the sixth hour 0·9 cub. centim., and in the seventh hour 0·7 cub. centim. The iron appears to be now nearly exhausted, after the extrication of 63·1 cub. centims., or 12·55 volumes of gas.

It is evident that iron cannot be safely dealt with in experiments upon the permeation or upon the absorption of gases, till these gases, whether self-produced or preexisting, are first extricated from the metal. The carbonic oxide observed in the tube experiments of M. DEVILLE may have been derived from the same source*.

4. To observe the absorption of hydrogen, the mass of exhausted iron wire remaining after the last experiment was heated to redness, and cooled gradually in the same gas. The metal was afterwards freely exposed to air (as usual) to get rid of any loosely attached hydrogen. Now exhausted again by the Sprengel pump at a low red heat, the iron gave 2·5 cub. centims. of gas in one hour, but the greater portion in the first ten minutes, consisting of

---

* The gases which escape from cast iron in a state of fusion have been examined by M. L. CAILLETET. They appear to contain from 49 to 58 per cent. of carbonic oxide, 34 to 39 of hydrogen, and 8 to 12 of nitrogen.— Comptes Rendus, t. lxi. p. 850 (1865).

2·3 cub. centims. Hydrogen.

0·2 „   „   Carbonic oxide, &c.

——

2·5

The iron appears therefore to be capable of holding 0·46 volume of hydrogen. The wire became white, like galvanized iron. This was confirmed in a second observation, a thicker wire holding 0·42 vol. hydrogen.

5. The same specimen of iron was now charged with carbonic oxide gas, in the manner it had previously been charged with hydrogen. It was also freely exposed to air. The iron wire remained soft, was not capable of becoming hard when heated red-hot and suddenly cooled, and was not altered in aspect or in solubility in acids. The gas extricated by the air-exhauster amounted to

9·45 cub. centims. in 13 minutes.

2·43 „   „   5   „

8·05 „   „   42   „

3·15 „   „   60   „

——

23·08 „   „   in two hours.

Of this gas 20·76 cub. centims. proved to be carbonic oxide. *Pure iron, then, is capable of taking up at a low red heat, and holding when cold,* 4·15 *volumes of carbonic oxide gas.* This fact was confirmed in various other experiments. It explains partly, if not entirely, the abundance of carbonic oxide observed among the natural gases of iron in experiments 1, 2, and 3. In the course of its preparation wrought iron may be supposed to occlude six or eight times its volume of carbonic oxide gas, which is carried about ever after. How the qualities of iron are affected by the presence of such a substance, no way metallic in its characters, locked up in so strange a way, but capable of reappearing, under the influence of heat, at any time, with the elastic tension of a gas, is a subject which metallurgists may find worthy of investigation.

The relations of the metal iron to carbonic oxide gas appear to be altogether peculiar. They cannot fail to have a bearing upon the important process of *acieration*. The intervention of carbonic oxide in the usual process of the cementation of iron with charcoal, long recognized by accurate observers, may be said now to be placed beyond all doubt by the recent beautiful research of M. MARGUERITTE[*]. Hitherto the decomposing action of the iron upon carbonic oxide has been supposed to be exercised only at the external surface of the metal. A surface-particle of the iron has been supposed to assume one half of the carbon belonging to an equivalent of carbonic oxide ($C_2 O_2$), while the remaining elements diffused away into the air as carbonic acid ($C O_2$), to reacquire carbon from the charcoal placed near, and to become capable of repeating the original action. It is now seen that such a process need not be confined to the surface of the iron bar, but may occur throughout the substance of the metal, in consequence of the prior penetration of the metal by carbonic oxide. The direct contact and action of

——

[*] Annales de Chimie, &c., 4 sér. t. vi., 1865.

carbon (in the form either of diamond or charcoal) upon iron is allowed to produce cast iron and not steel. It appears that the diffused action of carbonic oxide is the proper means of distributing the carbon throughout the mass of iron. The blistering of the bar appears to testify to the necessary production and evolution of carbonic acid, owing to the decomposition of the carbonic oxide in the interior of the bar.

The inquiry suggests itself whether acieration would not be promoted by alternation of temperature frequently repeated. The lowest red heat, or a temperature even lower, appears to be most favourable to the absorption of carbonic oxide by iron, or for impregnating the metal with that gas; while a much higher temperature appears to be required to enable the metal to decompose carbonic oxide, to appropriate the carbon, and become steel. The action of a high temperature is made very clear by M. MARGUERITTE. The process of acieration, it seems then, should be divided into two distinct stages, conducted at very different temperatures,—the first to introduce carbonic oxide into the iron, and the second to decompose the carbonic oxide so introduced. The carbonic oxide once safely occluded by the iron, the metal might even be cooled and preserved in the air, the second heating being postponed for any length of time. Such alternations of temperature are not unlikely to occur by accident during the usual long process of cementation; but they might be properly regulated with advantage, and the process may admit of being abridged in point of time.

Antimony, as a highly crystallizable metal, was exposed to hydrogen gas both above and below the point of fusion of the metal, and afterwards submitted to exhaustion in the usual manner. No hydrogen was extricated.